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**Conference Report**

**INTERNATIONAL WORKSHOP ON LIGHT EMISSION  
AND ELECTRONIC PROPERTIES OF NANOSCALE SILICON  
UNC-CHARLOTTE  
CHARLOTTE, NC 28223**

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## PREFACE

This document contains the proceedings of the International Workshop on Light Emission and Electronic Properties of Nanoscale Silicon, held at the CC Cameron Applied Research Center of UNC - Charlotte, Feb. 1-3, 1993. The main purpose of this workshop, unlike others on porous silicon, was to bring together researchers on two aspects of nanoscale silicon referred to by M. Tompsett (US Army Res. Lab.) as "accidental and deliberate nanostructures". The former is inexpensive with poorly defined structure and luminesces well, and the latter, expensive with well defined structure and to date luminesces poorly. Research during the last few years into photoluminescence from porous silicon and other nanoscale silicon structures clearly demonstrates that, unlike bulk silicon, nanoscale silicon has the potential to be an optical source for optoelectronic applications. Realization of this potential requires an efficient method *for electrical excitation of the luminescence*, which may require substantially different conditions than those resulting in efficient photo-excited luminescence. This workshop assembled significant recent research in electronic transport and luminescence in nanoscale silicon structures, together with a diverse selection of fabrication techniques, in order to begin to address the critical physics and fabrication issues in using this exciting new material for optoelectronic applications. More than 40 papers were presented dealing with experiments, characterizations and theories. The workshop was opened by a presentation on the perspective for payoff from research on nanoscale silicon by G.J. Iafrate (Director of ARO) and M. A. Stroscio (ARO), and a review of quantum confinement by R. Tsu. The team who first demonstrated quantum confinement in porous silicon was represented by U. Gosele (Duke Univ.). A total of 13 papers were devoted to the mechanisms of photoluminescence in porous silicon. There were 11 papers on nano-fabrication such as Silicon Toothpicks by R. B. Marcus



(NJ Inst. of Tech.). Transport properties were led off by M. Reed (Yale Univ.) on quantum dot resonant tunneling and followed by E. Nicollian and R. Tsu (UNC -Charlotte) on transport via tunneling through nanoscale silicon embedded in a-SiO<sub>2</sub> matrix. Theories were represented by B. Delley (Paul Scherrer Inst.), M. Hybertsen (AT & T Bell), G. Sanders (Univ. of Florida) and D. Babic and R. Tsu (UNC -Charlotte). The last item presented the drastically increased binding energy of shallow impurities for nanoscale silicon. The consequence is far reaching because extrinsic conduction ceases in nanoscale silicon making it difficult to excite electroluminescence. There were 3 papers on device potentials led off by J.F. Harvey (US Army Res. Lab.) on what are important rules in developing light emitting devices. An impressive electro-luminescence device consisting of a n-SiC/ps/p-SiC structure was fabricated at Nippon Steel Corp. by T. Matsumoto, as well as an ITO device fabricated by F. Namavar (Spire Corp.). We believe the superior performance of the Nippon device is partly due to the matching of the dielectric constant of the reduced value for nanoscale silicon (Modified Penn model of R. Tsu and L. Ioriatti) to the dielectric constant of SiC resulting in the elimination of the induced charges which are responsible in the bulk of the increase in the binding energy of donor levels. (see D. Babic of this report). At any rate, it is the subjective view that Matsumoto's result indeed has given us hope of a practical device. There were 3 papers dealing with chemical species as the possible origin of the strong luminescence, led off by M. Brandt's (Max-Planck Inst. Stuttgart) paper on Siloxene. There were two unusual "presentations", one by Brown (Univ. of Rochester) on isoelectronic impurities, and the other by J. Harvey on a collection of papers whose authors were unable to attend our workshop! We have also included 2 rather unique ways of producing nano-particles of silicon, the pyrolysis of greatly diluted disilane presented by L. Brus (AT & T Bell) and direct chemical synthesis of nanoscale silicon by N. Matsumoto (NTT Res. Lab.).

This volume also includes reports of discussion sessions dedicated to a number of issues:

- |   |                  |
|---|------------------|
| <b>ELECTRICAL TRANSPORT IN NANOSCALE Si STRUCTURES</b><br>Limits of Lithography, Lack of averaging, other limitations?  | Mark Reed        |
| <b>LUMINESCENCE IN Si-NANO PARTICLES</b><br>Pressed or embedded in a matrix, chemical stability and defects?  | Louis Brus       |
| <b>MECHANISM FOR LUMINESCENCE IN QUANTUM CONFINED Si</b><br>What happens to the indirect gap, transition matrix elements, quantum confinement, surface effects? | George Wright    |
| <b>CHARLOTTE STANDARD</b><br>Comparison of Luminescence Efficiency  | R. Tsu           |
| <b>ROLE OF NANOSCALE Si-DEVICES</b><br>Can we dope, in a matrix? Advantage and disadvantage?  | Nancy Heagel     |
| <b>DEVICE APPLICATIONS</b><br>Optoelectronic injection devices? Electroluminescence?  | Mike Tompsett    |
| <b>WHAT HAVE WE LEARNED</b><br>Among these above, summaries by M. Reed, L. Brus, M. Tompsett, N. Haegel, R. Tsu and P. Fauchet are included.                    | Philippe Fauchet |

The results of this workshop are very encouraging with regard to the prospects of optoelectronic applications of nanoscale silicon. The range of color available from electrically or photo excited luminescence spans the visible and near IR. Luminescence bands with different time constants have been observed, with some time constants less than a nanosecond. Physical models of the luminescence and electrical transport in these nanostructures are advancing and explaining a wide range of the observed phenomena. Microanalysis and very recent Electron Paramagnetic Spin Resonance results have clarified the physical structure of porous silicon. Techniques for electrical excitation of the luminescence have been demonstrated with improved efficiencies. Better understanding of the physical structure and electrical properties of porous silicon have produced a number of promising proposed techniques for electrical contact and electrical excitation. VLSI fabrication techniques have been developed, and simple IC's using porous silicon elements have been demonstrated. Oxidation techniques have been demonstrated

which substantially improve the chemical and environmental stability of porous silicon luminescence, even in cathodeluminescence. A wide variety of alternative techniques to fabricate nanoscale silicon structures were demonstrated, including the chemical synthesis of nanoscale silicon particles with tightly controlled size distributions. Luminescence has been demonstrated in most of these structures, and they make possible experiments with much better control of external and chemical factors. Novel device structures have been proposed for several of these structures and will undoubtedly be attempted in the next year. Many of the problems noted in early porous silicon research are being overcome. Physical understanding, fabrication technology, and device ideas for porous silicon are coming together in a highly auspicious manner. In addition, techniques for fabricating alternative nanoscale silicon structures are coming on line. Together, these results are very promising for the prospects of nanoscale silicon in optoelectronic circuits.

The organizers wish to thank all the authors, participants, session chairs and discussion moderators for making this workshop a success. We are especially grateful to Ms. Pamela Caggiano for her help in nearly every phase of this workshop. Finally, we want to gratefully acknowledge the following sponsors:

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Raphael Tsu  
James F. Harvey  
Louis Brus  
John Zavada  
John Prater  
Harry Leamy

April 1993

I.

## INTRODUCTION

**Synopsis of Keynote Address:**  
**Perspective on Potential Payoff from Research on Nanoscale Silicon**  
presented at the  
International Workshop on Light Emission and Electronic  
Properties of Nanoscale Silicon  
University of North Carolina at Charlotte, February 1, 1993

Gerald J. Iafrate  
Director  
U.S. Army Research Office

Michael A. Strosio  
Senior Research Scientist  
Office of the Director  
U.S. Army Research Office

Historically, the U.S. Army's investment in research relating to the electronic properties of silicon as well as to process modeling, computer aided design and device architectures has produced a many-fold return on investment. A very conservative estimate of Department of Defense cost savings made possible by silicon-related research is in the billions of dollars. The enormous impact of federally supported research related to silicon technology is illustrated clearly by an examination of the National Academy of Engineering's list of the ten outstanding technological achievements of the twenty-five year period from 1964 to 1989 [1]; these achievements are: moon landing; application satellites; microprocessor; computer aided design and manufacturing; computer-aided tomography; advanced composite materials; jumbo jet; lasers; fiber optic communication; and genetically engineered products. More specifically, at least half of these landmark achievements were made possible, in part, by U.S. Army and U.S. Department of Defense research which led to fast Fourier transforms, SPICE (Simulation Program with Integrated Circuit Emphasis), SUPREME (Stanford University Process Engineering Models), fundamental elements of computer-aided design technology, and applications of nonlinear shift register sequences. The U. S. Army has benefitted greatly from this research through reduced costs and increased functionality of Army electronics as well as through a wide range of applications such as secure communications and specialized signal processing tasks. Clearly, the U.S. government's support of silicon technology has yielded a many-fold return on investment.

Today, as a result of the discoveries of many of you at this international gathering, it is becoming increasingly clear that numerous potential technology advancements are being fostered by research on light emission and electronic properties of nanoscale silicon. Indeed, research on resonant tunneling due to quantum confinement effects in microcrystalline silicon [2,3] may lead to revolutionary advances in speed and dramatically reduced energy consumption of silicon electronics. Of perhaps even more far-reaching consequence, is recent research on silicon quantum wires [4] which exhibit photoluminescence at room temperature; clearly,

porous silicon structures could open a vast array of opportunities for incorporating optoelectronic functions in silicon technology. Recognizing the revolutionary potential of this possibility, the U.S. Army Research Laboratory has teamed with researchers supported by the U.S. Army Research Office to report the first [5] Raman spectra measurements and high pressure optical investigations of porous silicon; these investigators were also [5] among the first to use transmission electron microscopy to identify crystalline planes in microcrystallites of silicon. Potential U.S. Army technology advancements from research on porous silicon cover the gamut from ultrasmall integrated multifunctional sensors for monitoring the soldier's environment to smart structures and integrated sensors for more reliable, survivable, and efficient platforms and systems. Additional potential payoffs include high data rate photonic communications as well as miniaturized computers and displays.

History has shown that the anticipated payoffs from basic research are difficult to predict for more than about a decade into the future; however, if the benefits from research on porous silicon are only a thousandth of those from past research on silicon, the return on investment will be enormous.

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## QUANTUM CONFINEMENT: FROM INVERSION LAYER, SUPERLATTICE AND QUANTUM WELL TO POROUS SILICON

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The discovery of intense luminescence in porous Si represents the manifestation of quantum confinement from silicon inversion layer, superlattice and quantum well to porous silicon. The role of dielectric constant in nanoparticles is discussed.

Schrieffer considered the possibility of quantization in a Si-inversion layer<sup>1</sup> and concluded that surface scattering results in a continuum. However Greene<sup>2</sup> proceeded to investigate the consequence of quantization. The experimental confirmation soon followed<sup>3,4</sup>. In 1969<sup>5</sup> and 1970<sup>6</sup>, Esaki and Tsu proposed the fabrication of man-made superlattices as a means to control quantum states. A single isolated quantum well was born when better understanding of transport in superlattices was investigated on the basis of tunneling<sup>7</sup>. The subsequent experimental observation of resonant tunneling through a single quantum well<sup>8</sup> led to the investigation of the optical studies of isolated quantum wells<sup>9,10</sup>. These early works on quantum confinement have led to discoveries such as the quantum Hall effects<sup>10</sup> and fractional quantum Hall effects<sup>12</sup>, as well as important technologies<sup>13</sup> such as resonant tunneling devices, functional devices and tailor-made injection lasers.

Recently, Canham<sup>14</sup> has reported intense luminescence in anodically etched silicon attributed to quantum confinement. The shift of the absorption edge reported by Lehman and Gösele<sup>15</sup> was further corroborated by the correlation of the up-shift of the luminescence peak with the down-shift of Raman phonons indicating quantum confinement<sup>16</sup>. As a result of many discussions during this workshop, it is clear that quantum confinement plays a leading role in the reported luminescence.

Another recent development is the observation of coulomb blockade in the tunneling through a small Si particle where the extreme small size of the capacitance results in the charging voltage per electron in the range of a fraction of a volt, many times greater than  $kT$  at room temperature. The conductance versus voltage is a series of peaks separated by the charging voltage<sup>17</sup>. The term Coulomb Blockade represents discrete charging of localized states or quantum confined states of the nanoscale particle.

As the particle size decreases, the dielectric constant of the nanoscale particle is significantly reduced<sup>18</sup> leading to carrier freeze-out at room temperature because of the increase in the binding energy of shallow doping levels. This mechanism serves as a self-limiting process for the anodic etch because etching is stopped when carriers disappear. At a radius of 1.2nm, dielectric

constant is reduced by a factor of two, so that the binding energy should be increased by a factor of four. However, it was found that the binding energy is increased far more due to the attractive interaction of the electron with the induced positive charge of the donor at the dielectric interface<sup>18</sup>. Since the high dielectric constant of water results in induced charges of opposite sign, electrolyte such as water decreases the binding energy resulting in better conduction. Therefore, the observed efficient electroluminescence in the electrolyte<sup>19</sup> may be caused by the reduction of the binding energy. It should be possible to minimize the increase in the binding energy of dopants by a proper choice of the dielectric constant as a matrix or as contacts.

The recent doubts raised<sup>21</sup> regarding the efficient luminescence in porous silicon is at least consistent with the traditional disbelief of quantum confinement from Si-inversion to superlattice and quantum well. This sort of negative attitude is quite understandable in view of the difficulty in experimental proof. At present, the prevailing view is that quantum confinement represents an important mechanism of the efficient luminescence in porous silicon.

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II.

## POROUS SILICON - EXPERIMENTAL

## **SELF-LIMITING FORMATION OF POROUS SILICON QUANTUM SPONGE STRUCTURES: CONSEQUENCES AND OPEN QUESTIONS**

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The dissolution of crystalline silicon in hydrofluoric acid (HF) requires the supply of electronic holes from the silicon substrate. In p-type silicon these holes are available as majority carriers and allow etching until the formation of sufficiently small remaining silicon structures between the pores lead to quantum confinement, a larger bandgap and to the prevention of a supply of holes from the bulk silicon. This leads to a sponge-like silicon structure ("quantum sponge") by a self-limited etching process due to quantum confinement [1-7]. As a consequence of this process the size of the interconnected columns and therefore also the bandgap (which finally determines the upper limit of the frequency which can be reached by photo- or electroluminescence) can be controlled by a proper control of the hole supply. Smaller structures are obtained in a self-adjusting way by increasing the current density or the HF concentration provided electro-polishing can be avoided. Another way - besides chemical after-etching [8] which is inherently not self-limiting - and basically the only way for n-type silicon to get smaller structures is illumination with light of sufficiently high energy. Illumination with light in the proper frequency range allows to overcome the limitation in size (at least for a surface layer) otherwise imposed by the competing process of electro-polishing.

Finally, some comments will be made on open problems in contacting porous silicon devices and on possibilities to generate regular arrays of vertical quantum wires (instead of the interconnected quantum wires in a typical quantum sponge structure).

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# ROOM AND LOW TEMPERATURE RADIATIVE AND NON-RADIATIVE MECHANISMS OF PHOTO- AND ELECTRO-LUMINESCENCE OF POROUS SILICON, THE IMPORTANCE OF OXIDE PASSIVATION

S. Billat, A. Bsiesy, G. Fishman, F. Gaspard, R. Hérino, M. Ligeon, I. Mihalcescu, F. Muller R. Romestain, J.C. Vial; CNRS + Université Joseph Fourier de Grenoble France and R. M. Macfarlane, IBM almaden Research center San José California USA.

Beside the quantum confinement effect, inside nanometer sized silicium structures, which explains the visible light emission, the electrochemistry has a dramatic effect the non-radiative processes and then controls the brightness of the light emission, at room temperature, via the nanometer sized surface passivation. In addition to bestowing good mechanical properties and stability to the porous silicon structure, the passivation by anodic oxidation in water is now a well controlled technique which allows a better control of the parameters than the classic hydrogen passivation in HF. It is also possible to take advantage of the "wet" intense electroluminescence which occurs during the anodic oxidation process. The level of oxidation turns out to be a critical parameter for the non-radiative de excitation of photo- and electro-luminescence. This can be explained by the limitation of the escape of carriers from the confined zone to non-radiative centers. More quantitatively, a description of the carrier escape by tunnelling through the passivated layer accounts well for experimental observations as different as: (i) fluorescence decay time dependence on confinement or level of oxidation, (ii) quantum efficiencies of photo- and electro-luminescence, (iii) temporal evolution of photo- luminescence after pulsed

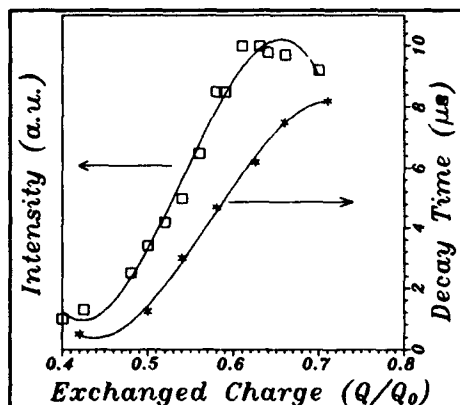


Figure 1

Room temperature decay times and photoluminescence intensities as function of anodic oxidation level for samples of 65% porosity detected at 700 nm. The parallel evolutions indicate that the non-radiative processes are dominant at room temperature ( and above)

excitation, (iv) above room temperature dependence of the quantum efficiency and lifetime, (v) time dependence of the "wet" electro-luminescence. The passivation has also to be taken into account for a complete description of the "famous" blue shift which occurs during the porous silicon processing. The success of this unique model allows its use for the predictions of optical properties of various porous silicon structures in vu of practical applications.

At lower temperature, the evolution of the radiative recombination rates has to be considered, simultaneously with the non-radiative contribution, to explain the dramatic increase in the luminescence lifetime associated with the reduction of the quantum efficiency. A thermal redistribution of populations among excited states with allowed and forbidden

radiative transitions is the proposed model. It is shown that the energy splitting of the excited state is consistent with the exchange interaction between confined electron and hole in nanometer sized quantum dots.

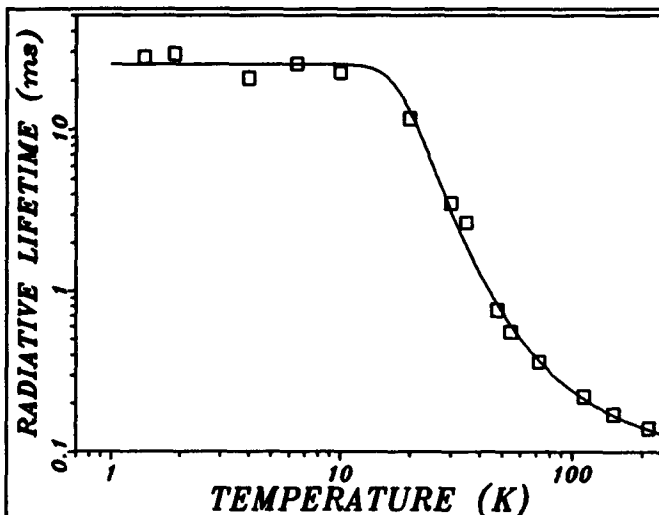


Figure 2

temperature dependence of the radiative lifetime . The solid line is the best fit of the experimental data following the model shown in fig 3 with  $\Delta E=10$  meV,  $\tau_2=25$  ms and  $\tau_1=22\mu s$ .

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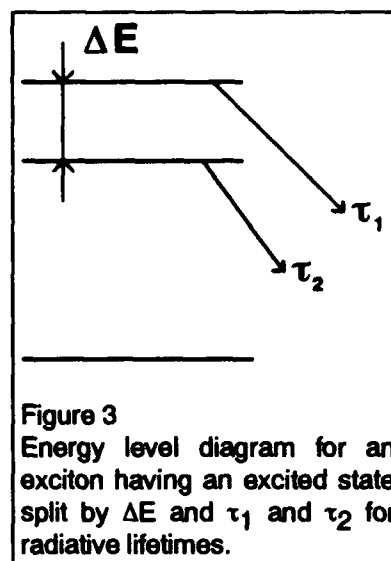


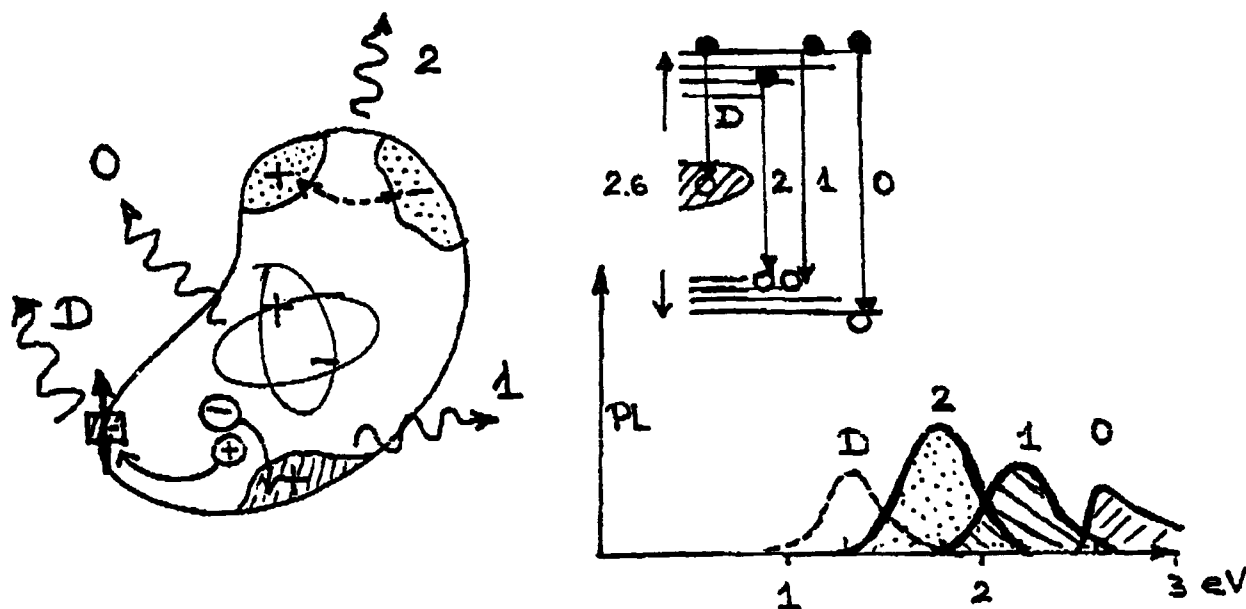
Figure 3  
Energy level diagram for an exciton having an excited state split by  $\Delta E$  and  $\tau_1$  and  $\tau_2$  for radiative lifetimes.

**THE SURFACE-STATE-EMISSION MECHANISM-  
A UNIFIED MODEL OF THE INFRARED, SLOW AND  
FAST VISIBLE LUMINESCENCE BANDS OF NANOCRYSTALLINE SI**

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The luminescence emission from porous Si falls into three spectrally distinct bands with characteristically different response times. Time-resolved luminescence experiments have allowed the identification of a fast and slow visible luminescence band [1,2]. In addition, there exists an infrared band that strongly grows with decreasing temperature [3]. For conventional, microporous Si the bands each have a width of order 0.4 eV and are centered about 2.3 eV, 1.8 eV and 1.2 eV.

The surface-state emission model [4,5] offers a unified explanation of these. The model invokes tail states in the energy spectrum of the quantum particles capable of trapping binding length is of order 0.5-1 nm. Luminescent recombination occurs in a hierarchy of processes involving 0, 1 or 2 of the trap states. As in the figure, we argue that emission results when the photoexcited geminate pair recombines directly (0-band), via trapping of one partner (1-band or both (2-band)). In addition, the existence of a dangling-bond deep level is expected to give an infrared emission (D-band) at one-half the energy gap. The model describes a fast, blue-green emission (2.2 eV), a slow red light component (1.8 eV) and the relatively fast, infrared D-band (1.3 eV). The transitions are sketched in the figure for an assumed  $E_g$  of 2.6 eV and a surface localization energy of 0.4 eV.



There is an interesting analogy of the fast and slow visible emissions for porous Si to those of a-Si:H [6].

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# Optical and Electronic Properties of Luminescent Porous Silicon

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On the basis of our previous studies of porous silicon (PS) concerning the photoelectrochemical activity [1-4], photoconduction [5], photo- [6-8] and electroluminescence [9,10], optical absorption [7], and electrical conduction [11], we report here some experimental data on the electronic structure of PS in terms of reflectance spectra, UPS, and EPR. Recently observed electrical PL quenching is also presented.

The PS layers were formed by anodization of nondegenerate p- and n-type Si wafers in aqueous or ethanoic HF solutions at current densities of 10-200 mA/cm<sup>2</sup> for 5-180 min in the dark or under illumination. For measurements of the intrinsic nature of PS (such as EPR), self-supporting PS films were prepared [7].

The electronic structure of PS was optically characterized by a combination of spectroscopic ellipsometry and synchrotron radiation (SR) reflectance spectra measurements. Microscopic effects of illumination after anodization on the PL mechanism were investigated by SR-excited UPS analyses. Paramagnetic centers in PS films, separated from Si (100) and (111) wafers after anodization, were studied by EPR at room temperature. Effects of the external electric field on the PL characteristics were also studied for PS formed on p- and n-type wafers.

Major results are summarized as follows:

1. Optical constants spectra of PS preserves the fundamental feature of crystalline Si [11,12].
2. The PS absorption spectra obtained from the Kramers-Kronig analysis of SR reflectance data exhibits a blue shift of about 0.3 eV in comparison to those of crystalline Si (Fig. 1) [12].
3. Illumination after anodization results in the formation of oxides at the surface (Fig. 2), and it closely relates to a significant increase in the PL intensity [11,13].
4. The paramagnetic center in PS, which is an origin of the nonradiative relaxation channel, has C<sub>3v</sub> symmetry. The angular dependence of EPR lines indicates that this center is attributed to a dangling bond localized on a single Si atom [14].
5. For PS layers formed on highly doped wafers, the PL emission can reversibly be quenched by the external electric field [15].

These results suggest that luminescence of PS can be explained from the band scheme, and that complete surface passivation is a key parameter for efficient radiative recombination.

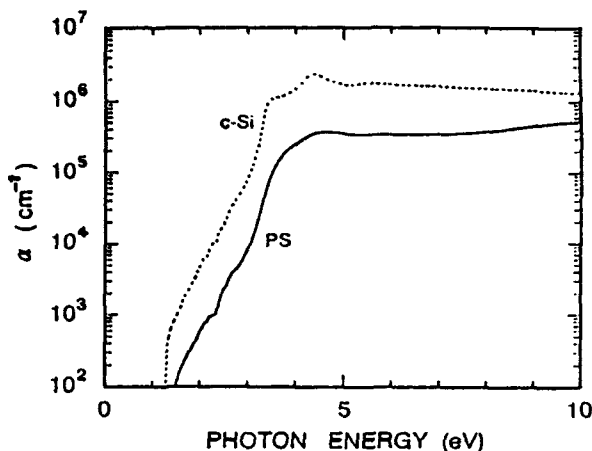


Fig. 1. Calculated absorption spectra of porous Si (PS: solid curve) and single crystal Si (c-Si: dashed curve).

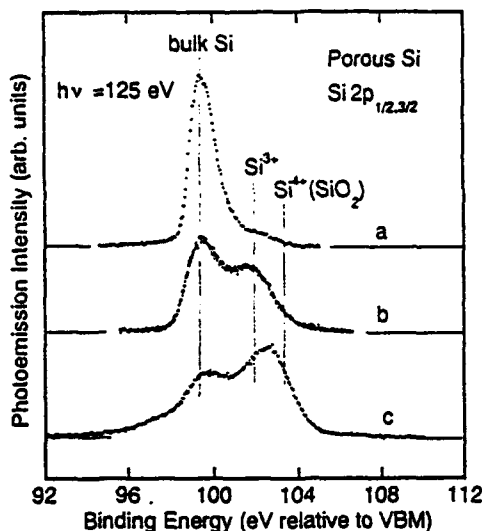


Fig. 2. UPS spectra of Si 2p for three PS layers formed on a p-type (111) Si substrate with a resistivity of 10-20Ωcm under different conditions. The binding energy is referred to the valence band maximum.

a: anodized in ethanoic 50% HF at 10 mA/cm<sup>2</sup> for 5 min.

b: anodized in ethanoic 50% HF at 200 mA/cm<sup>2</sup> for 5 min.

c: illuminated after anodization under the same condition as sample a.

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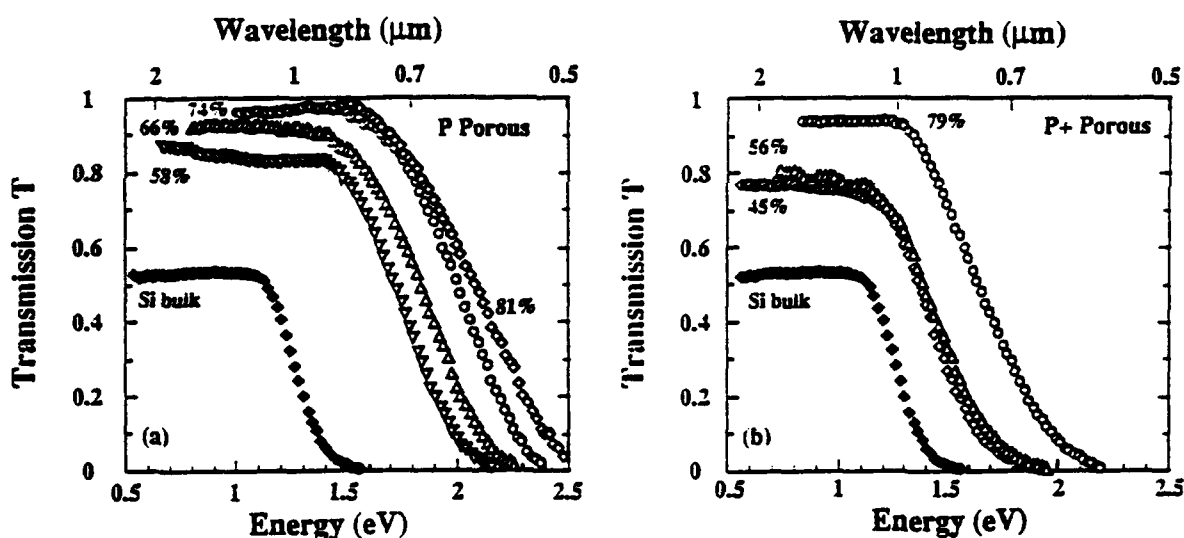
# OPTICAL AND ELECTRICAL PROPERTIES OF POROUS SILICON

I. Sagnes, D. Bensahel, G. Bomchil, F. Ferrieu, A. Halimaoui, P. Perret, J. L. Regolini, G. Vincent,\* and P. A. Badoz

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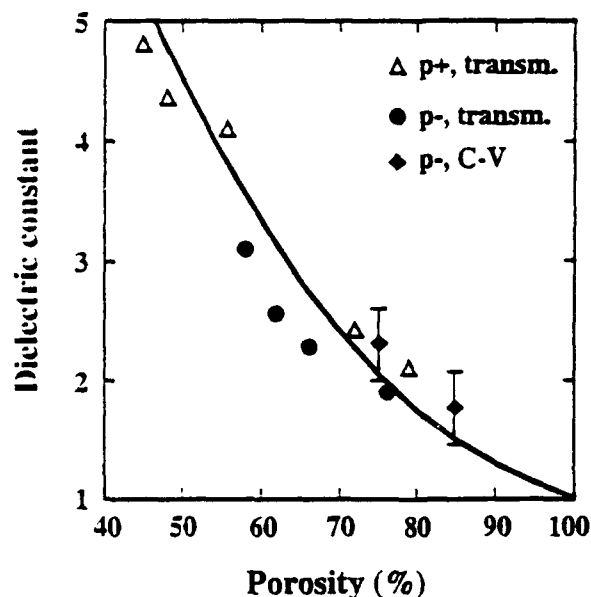
Results concerning the optical transmission of free standing photoluminescent<sup>1,2</sup> porous silicon (PS) films are presented: PS films of equivalent porosities but different microstructures,<sup>3,4</sup> and particularly, different nanocrystallite sizes<sup>5</sup> (i.e. a few nm when fabricated on p- substrates and a few 10 nm on p+) show markedly different transmission curves, i.e. blue shifted with decreasing crystallite sizes.<sup>6</sup> This size effect in PS absorption coefficient confirms the quantum size effect hypothesis concurrently proposed by Canham and Lehman and Gösele.



**Fig. 1:** Transmission coefficient vs. photon energy for 40  $\mu\text{m}$  thick free standing porous silicon films of different porosities and fabricated on a) p-type 1  $\Omega\text{cm}$  Si substrate, and b) p+ type 0.01  $\Omega\text{cm}$  Si substrate.<sup>6</sup>

The static dielectric constant of PS, deduced from the value of the transmission plateau  $T_0$  in the infrared region (by  $T_0 = 2n/(n^2+1)$  and  $\epsilon_0 = n^2$ ) is, however, only slightly affected by the microstructure, as shown in Fig. 2: The decrease in  $\epsilon_0$  with porosity is indeed well accounted for by the (classical) Bruggeman effective medium approximation, and this, independantly of the size of the PS nanocrystallites. This is further confirmed by capacitance-voltage measurements of  $\epsilon_0$  in metal/p-PS/Si heterostructures (filled diamond in Fig. 1).<sup>7</sup>

Fig. 2: Static dielectric constant of porous silicon as a function of porosity;  $\Delta$  and  $\circ$  are obtained from the transmission data of Fig. 1 (free standing PS films fabricated on p+ and p- Si substrate respectively),  $\diamond$  from capacitance - voltage measurements. The solid line is the static dielectric constant calculated with the Bruggeman effective medium approximation.



Finally, electro-luminescence characteristics of solid state PS based diodes emitting in the red are presented:<sup>7,8</sup> The EL spectra closely resemble those of PL, i.e. centered around 700 nm and with similar FWHM, and the quantum yield measured are between  $10^{-6}$  and  $10^{-5}$  depending on the PS structure used; preliminary dynamic measurements show that EL decay time are below 1  $\mu$ s (experimental time resolution), i.e. slightly faster than already published PL decay times.

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# ON THE DISTINCTION BETWEEN ELECTRONIC CORE- AND SURFACE- STATES OF NANOCRYSTALLINE SILICON

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## ABSTRACT

Visibly luminescing porous Si is known to consist of nanometersized crystalline Si regions covered with passivating SiH<sub>3</sub> or SiO<sub>2</sub> /1/ tissue. Models and mechanisms that explain the light emission by considering the surface-confined electronic states /2/ must independently identify and prove the existence of such states. The lecture explores the experimental facts relating to the electronic states associated with the bulk of the crystallites (core-states) and their surface-states.

For passivated surfaces of bulk crystalline Si (for example the Si-SiO<sub>2</sub> interface in MOSFETs), volume states are those of the well known band structure. The surface states, which are very few in this case, are of two types: shallow, band-edge states and deep, broken-bond levels. The mesoporous Si with crystallite size >60 Å, must have relatively more surface defects of both types, but the energy distribution of volume states is essentially unchanged. This material does not show visible luminescence. For nanoporous Si, in which the crystallites are smaller than 50-60 Å, 10 to 20% of the Si atoms are in the surface layer. At the same time the energy gap between core-states is dramatically increased. Both facts lead us to expect an increased importance of states confined on the surface and with energies lower than those of the core-states. Ref.3 has identified such states in tight-binding calculations for the reconstructed ideal surface of a thin Si slab. Disorder and structural irregularities will cause additional surface-states in the enlarged gap. We discuss the following experiments on nanoporous Si (as-prepared or rapid thermal oxidized) that identify surface states:

- electronic absorption measurements in the spectral region 0.6-5 eV
- electronic paramagnetic resonance (EPR) studies
- comparative IR- and Raman spectroscopy of the Si-Si vibrations
- PL energy position shift without changing crystallite size
- PL quenching by deep defects.

The results support the explanation of the luminescence involving surface states.

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## **RECENT POROUS SILICON RESEARCH RESULTS AT THE NATIONAL RENEWABLE ENERGY LABORATORY**

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### **I. A New Approach to Quantum Confinement with Applications to Porous Si<sup>1</sup>**

A simple truncated-crystal approach has been used to calculate the electronic structure of finite crystals. In this approach, energy levels of the crystal are given by  $\epsilon_{TC} = \epsilon_{bulk}(\kappa^*)$  where  $\kappa^*$  is a subset of the bulk  $k$ -vectors determined by the size and shape of the crystal. Going beyond the effective-mass model, this method includes the potential energy through a (possible) nonparabolic energy dispersion  $\epsilon_{bulk}(\kappa)$ , hence it can be applied to mesoscopic small systems. Applying this method to porous Si, it is found that quantum confinement alone is not sufficient to give rise to any direct-indirect gap crossover nor any sizable enhancement in optical matrix elements for wire and dot structures with dimensions larger than 1 nm.

### **II. Enhancement and Stabilization of Porous Silicon Photoluminescence by Oxygen Incorporation with a Remote-Plasma Treatment<sup>2-4</sup>**

We have developed a treatment that enhances and stabilizes the photoluminescence (PL) from porous Si films. Films prepared by anodization in a 50% HF/ethanol solution were annealed at 450°C in vacuum, exposed to air, and then exposed to a remote-hydrogen plasma. Infrared absorption spectroscopy revealed that the concentration of oxygen, rather than hydrogen, was increased by the processing steps, and that SiH<sub>2</sub> species had been eliminated from the surface. The PL from treated films was initially ~30 times more intense than from the as-etched films. The PL intensity increased with illumination time in air until a steady-state intensity was reached.

### **III. Properties of Photodiodes with Porous Si Light Absorber or Surface Layer<sup>5,6</sup>**

We have investigated the transport properties of p-type Si/porous Si/Au devices. The external quantum efficiencies of these devices can be greater than 20%, and the shape of the photocurrent spectra suggests that carriers photogenerated within porous Si can be collected in an external circuit. We also

studied the anti-reflection properties of point-contact Si solar cells with porous Si on the front surface.

#### **IV. Porous Si Nanostructure Revealed by Electron Spin Resonance<sup>7</sup>**

The anisotropy of the ESR absorption in films of porous Si was studied by rotating the magnetic field about key axes of the film. The results tell us that the primary g-factor is only slightly greater than that of the dangling bond found in amorphous Si while linewidths are half as much. The g-values vary with angle very much as for the (100) P<sub>b</sub> Si dangling bond center with no evidence for back-bonded oxygen.

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## Photoluminescence Excitation Spectroscopy of Porous Silicon

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Photoluminescence excitation (PLE) spectroscopy has been used to obtain the excitation spectrum for the strong visible luminescence emitted by anodically etched porous silicon [1,2]. PLE can be used to monitor the absorption process leading to the emission of the luminescence. It is performed with standard optical equipment and does not require removal of the porous silicon layer from the substrate.

Typical PL and PLE spectra are shown in Figure 1. Samples were prepared by anodic etching of 15  $\Omega$ cm p-type silicon in a HF/ethanol mixture for varying periods of time. The luminescence for this particular sample had a peak position of  $\sim 1.9$  eV. The PL was monitored at either the peak of the luminescence or on the low energy side in order to extend the range of the PLE spectrum. We observe two absorption edges in the room temperature PLE. The low energy onset occurs at approximately 2.0 eV and shifts to higher energy with post-etching storage time. A second onset begins at higher energy and rises rapidly into the ultraviolet region, consistent with the observation of strong luminescence from porous silicon samples under ultraviolet lamps. The evidence for two absorption onsets is displayed most clearly when the data are plotted on a logarithmic scale (Figure 2). The Stokes shift between the PL and the absorption onset appears to be very small, in agreement with recent PL results by Calcott et.al. [3].

The optical density,  $\alpha x$ , plays an important role in the interpretation of the PLE spectrum. If the optical density is large, all the incident light is absorbed and the PLE intensity is independent of the absorption coefficient. Information on the energy dependence of the effective absorption coefficient for luminescence can only be obtained in the "thin" limit, i.e.,  $\alpha x \ll 1$ , in which case the PLE signal is proportional to the absorption coefficient. It is also possible to move from the "thin" to the "thick" limit within a single PLE spectrum, since the absorption coefficient can vary by orders of magnitude over the energy range of interest. We believe that many of the differences that have been observed in the PLE spectra reported to date [4-6] are due to varying thickness of the samples, rather than reflecting fundamental differences in absorption behavior.

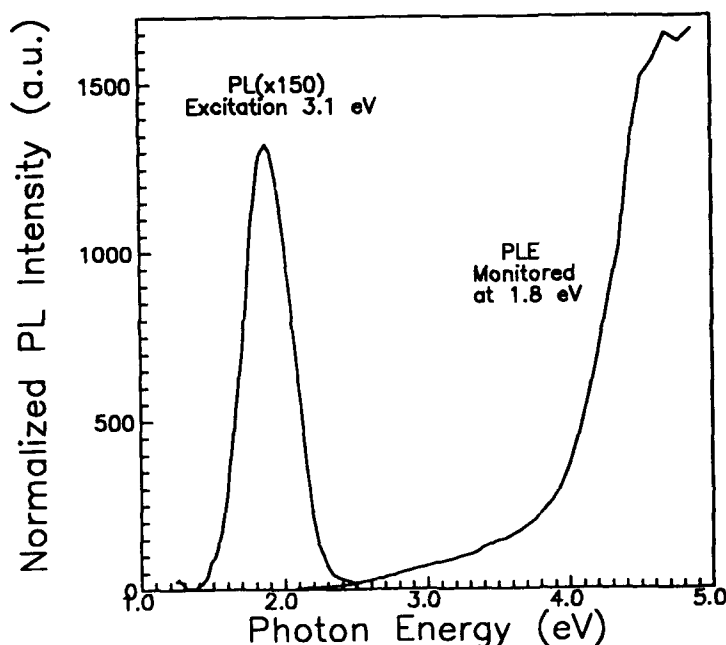


Figure 1

We have measured samples with varying thickness of the porous silicon layer. For the thinnest case (layer thickness  $\sim 1 \mu\text{m}$ ), we obtain an excitation spectrum which can be used to provide an excellent fit for the PLE spectra of thicker samples by simply adjusting the layer thickness [1]. This indicates that the sample meets the "thin limit" criterion over a wide energy range and can be used to obtain information on the energy dependence of the absorption coefficient. It is important to remember that PLE spectra reflect a combination of both absorption and recombination terms; but since PLE spectra of thick samples show fairly constant response for higher energies, it seems valid to assume that PLE spectra in the optically thin limit are dominated by changes in the absorption coefficient.

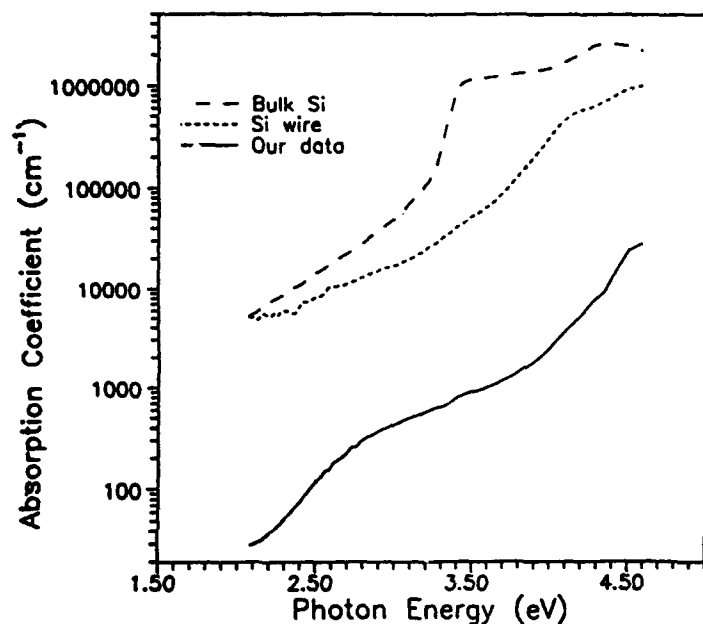


Figure 2

In Figure 2, we compare PLE data for porous Si with the absorption coefficient for bulk silicon and an absorption coefficient determined from  $\epsilon_2$  values in a recent calculation by Sanders and Chang for a quantum confined Si wire [7]. PLE data are taken from a sample demonstrated to be in the optically thin limit. Note that the effective absorption coefficient for the luminescence varies by almost three orders of magnitude between 2.0 and 4.5 eV. The value for the absorption coefficient has been derived from the PLE curve by assuming a layer thickness of  $1 \mu\text{m}$ . This explains the lower absolute values, since the actual effective thickness for the porous silicon is expected to be significantly less than the macroscopic layer thickness.

PLE results can be compared to absorption data obtained by standard transmission measurements of free standing porous Si layers [8,9] and to recent absorption data obtained by synchrotron measurements of reflectivity over a wide energy range [10]. Comparison of the porous silicon PLE spectra to absorption data for bulk silicon indicates that generation of carriers in bulk silicon is not the primary absorption mechanism involved in the PL process, though it may contribute to a varying degree depending on the sample. Although not exclusive of other hypotheses, the PLE results to date are consistent with a model involving absorption in quantum confined silicon structures leading to the production of visible luminescence in porous silicon.

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## Chemical and Physical Treatments of Light-Emitting Porous Silicon

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Canham's discovery [1] in 1990 that porous silicon could emit bright visible light has triggered worldwide activity [2,3]. One area of investigation concerns the origins of light emission and the other the possible device applications (e.g., LEDs). We have undertaken an extensive study of the effects of various chemical and physical treatments on the properties of light-emitting porous silicon (LEP<sub>Si</sub>). We are focussing on (i) the effects of chemical, electrochemical and physical treatments; and on (ii) the effects of processing steps encountered in a standard semiconductor fabrication line, such as annealing, thermal oxidation, ion implantation, various types of dry and wet etching, metallization, etc. The changes produced in LEP<sub>Si</sub> by these various treatments are characterized by optical techniques (e.g., cw and time-resolved photoluminescence, Raman scattering, FTIR), surface science techniques (e.g., XPS, SEM, STM, AFM), and electrical measurements in test device structures (e.g., photodetectors, LEDs). Important technological goals that include stabilization of the luminescence, tuning of the luminescence, and increase of the luminescence efficiency are achieved through an appropriate choice of treatments. What follows are examples taken from our recent work.

Figure 1 compares porous silicon prepared by electrochemical anodization in the dark and with light assistance. While the former samples show the usual hydrogen coverage, the latter show essentially no Si-H<sub>n</sub> bonds and a large number of Si-O bridging bonds. The improved stability of the PL of these samples is similar to what is observed after chemical or thermal oxidation of "normal" samples [4]. Further details can be found in Ref. 5.

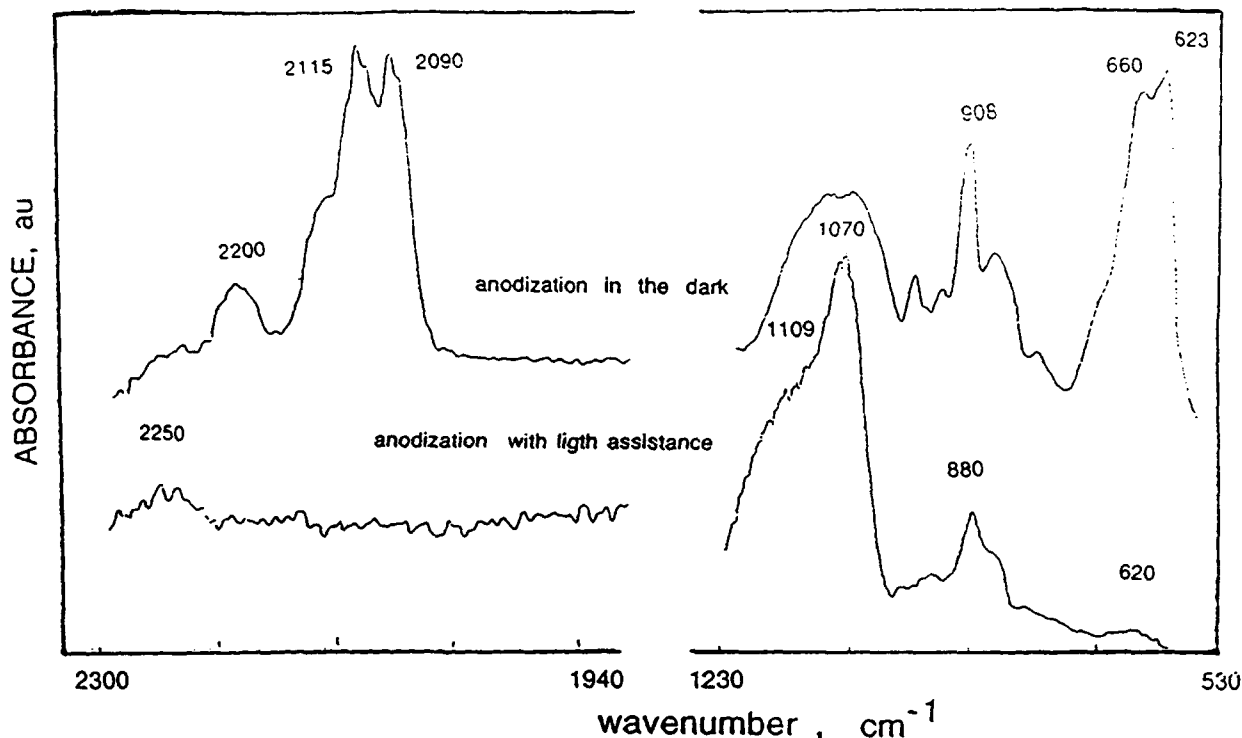
Figure 2 compares the PL intensity before and after ion implantation of porous silicon. Contrary to an earlier report that indicated that the PL was suppressed after ion bombardment [6], we find that implantation with P or B atoms does not change the PL intensity appreciably except at very high doses where amorphization is expected to take place in crystalline silicon. In fact, unexpectedly, the PL intensity even seems to increase at low doses. Note that self-implantation with silicon constantly decreases the PL intensity. It thus appears that implanting donors or acceptors has an effect that is substantially different from implanting with a neutral species (Si). Further details, including the PL lifetime and the effect of annealing after implantation, can be found in Ref. 7.

This work is the result of a collaboration between my students C. Peng, L. Tsybeskov and S. Duttgupta, Dr. G. Carver (AT&T Bell Laboratories, Princeton), Prof. Y. Gao and E. Ettegui (U. Rochester, Physics), Prof. S. Kurinec and F. Seyferth (Rochester Institute of Technology, Microelectronic Engineering), and Prof. G. McLendon and J. Rehm (U. Rochester, Chemistry). Support from Rochester Gas & Electric, Xerox, AT&T and the New York State Energy Development Authority is gratefully acknowledged.

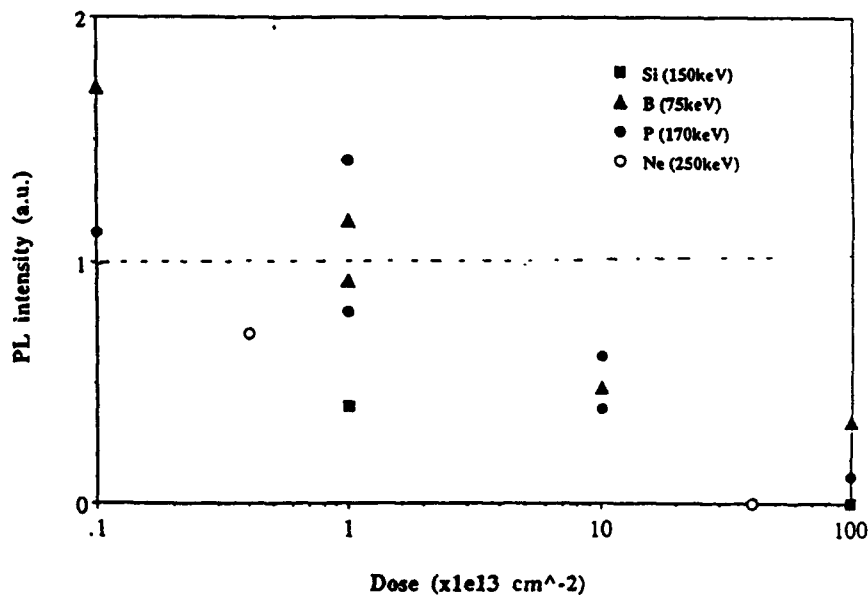


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**Figure 1** FTIR spectra of porous silicon anodized in the dark and with light assistance.



**Figure 2** Ratio of the PL intensity before and after ion implantation. Ne implantation data are from Ref. 6

## A Raman and Infrared Spectroscopic Study on Visible Light Emitting Porous Si

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A combined Raman scattering and infrared (IR) absorbance study on red light emitting porous Si (P-Si) (100-200 microns thick) was performed in this study. The experimental samples were prepared by an electrochemical process [1]. The heavy doped, p-type, 1-2 mm thick and (111) Si wafers with a resistivity between 0.02-0.04 Ohm·cm were adapted. After polishing and cleaning, the Si wafers were used to form porous layers by anodic dissolution and oxidation in HF acid on the highly polished side of the wafer using current densities of 70-100 mA/cm<sup>2</sup>, which is described in detail elsewhere [2]. The porous layer was removed from the substrate to form a porous Si membrane, which was typically 20-30  $\mu\text{m}$  thick or thicker (100-200  $\mu\text{m}$ ). The membranes display red light when illuminated white or flash light.

We performed a comparative Raman scattering study on these visible light emitting porous Si. Raman spectra from different samples, different spots on the sample, and from the front and back sides of porous Si membranes were compared. We made measurements at two temperatures (300 K and 80 K) and compared the temperature behavior of Raman features from porous Si with that from crystalline Si (c-Si) and microcrystalline Si ( $\mu\text{c-Si}$ ).

Porous Si membranes display their Raman spectra with the following features: (i) Porous Si possesses a characteristic Raman band, from 500 to 517  $\text{cm}^{-1}$ , at room temperature ( $\sim 300$  K), which is located below the 520  $\text{cm}^{-1}$  band of c-Si. This band varies from sample to sample and from spot to spot on a single sample; (ii) Its full width at half maximum (FWHM) is broader than the value of c-Si, is comparable with the value for  $\mu\text{c-Si}$ , and is much narrower than that of amorphous Si (a-Si); (iii) It down-shifts in frequency with a decrease of temperature in contrast with the temperature behavior for c- and  $\mu\text{c-Si}$ ; (iv) It broadens with a decrease of temperature with FWHMs less than that of the  $\mu\text{c-Si}$  at 300 K while being larger at 80 K; (v) The Raman features of porous Si are obviously different from that of a-Si. These features are shown summarily in Figure 1 and for more details in [3].

The anomalous temperature behavior of Raman spectra from visible light emitting porous Si may be explained by three possible mechanisms:

the soft mode theory, pore column network structure, and surface tensions. Most likely, based upon the free-standing quantum wire mode [1], porous Si possesses a high density of pore columns fixed in a solid network. As the sample cools down and contracts, the dimensional variations in two directions, perpendicular and parallel to the sample surface, may differ. Thus there may exist a lattice compression along the axis but a tension in the surface plane. This is similar to the case of a thin film with a small lattice constant deposited on a thick substrate with a large lattice constant, which leads to a down-shift of the optical phonon frequency [4].

The Infrared (IR) absorbance measurements on these samples exhibited a large number of IR (not Raman) active modes, indicating Si-Si, C-Si, C-O, Si-O, Si-H, O-H and complex vibrations. The X-ray photoemission spectroscopy also reveals the existence of Si, C, O and F in these samples [2]. This implies that the anodic etching produced a large area of Si surface, which were oxidized and organized to include the O-, H-, OH-, C-, CO- bonds and complexes along the pores, not being the pure siloxene ( $\text{Si}_6\text{O}_3\text{H}_6$ ). Our complementary study suggests that the free-standing Si-wires and Si-based polymer or organosilicon may both contribute to the visible light emission from porous-Si.

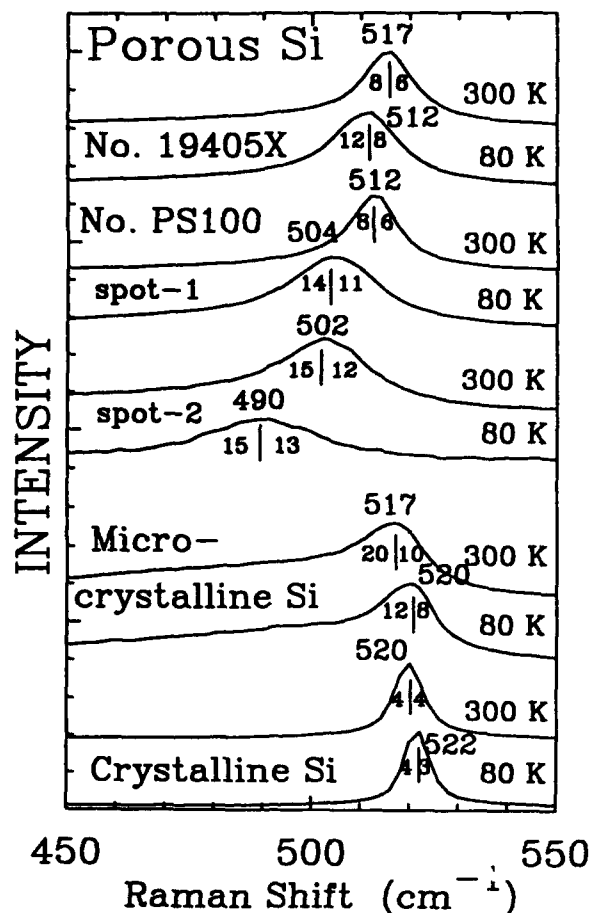


Figure 1 Comparative Raman spectra for porous,  $\mu$ c- and c-Si, taken at 300 K and 80 K.

\*Acknowledgements to S. Perkowitz, J. R. Payne and B. C. Covington.

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# Paramagnetic Defects at the Si/SiO<sub>2</sub> Interface of Oxidized Si Wafers and in Luminescent Porous Si.

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We have examined a paramagnetic defect in luminescent porous Si (LPSi) and determined that it is very much like the  $P_{b0}$  center of oxidized Si wafer surfaces. The porous Si defect, here termed  $P_{bu}$ , is present in very high concentration, up to  $10^{15}$  cm<sup>-2</sup>, or about a hundred times greater than ever observed on the oxidized wafer surface. This proves that the signal is from the PLSi, and it appears to reflect mainly the very large effective surface area of porous Si. The very strong signals allow easy study of important electron paramagnetic resonance (EPR) parameters. An example of a spectrum for LPSi on a (111) substrate is shown in Fig. 1. Hyperfine lines can be readily seen and measured.

For  $P_{bu}$ , the  $g$ -values, hyperfine structure ( $A$ ) from any <sup>29</sup>Si host nucleus, and superhyperfine structure ( $A_s$ ) from 3 neighboring Si nuclei are all very similar to  $P_{b0}$ :  $g_{||} = 2.0018$ ,  $g_{\perp} = 2.0085$ ,  $A_{||} = 156$  G,  $A_{\perp} = 84$  G,  $A_{s||} = 16$  G,  $A_{s\perp} = 12$ . The  $[P_{bu}]$  increases during low-temperature oxidation of the LPSi, and declines during H<sub>2</sub> anneal, in both cases just like  $[P_{b0}]$  on a wafer surface. Thus  $P_{bu}$  is rigorously identified as a surface defect and as a very similar variant of  $P_{b0}$ . In contrast to  $P_{b0}$  on [111] wafers, all limbs of the  $P_{bu}$   $g$ -map are evident, indicating that  $P_{bu}$  is situated on crystalline microfaces of several orientations. The  $P_{bu}$  disposition further shows that the porous Si skeletal structure is oriented like the wafer substrate lattice. Similar results were obtained for (100) wafer substrates, which support the (111) conclusions; but, since all  $g$ -limbs are seen on a (100) wafer, the conclusion would be less definitive for (100) alone.

The structure suggested for LPSi by EPR is shown in Fig. 2. The Figure shows a substrate of non-standard orientation, and is contrived to admit the possibility of microcrystallites of diverse character. Clearly, the EPR results do not support any detailed model. Nonetheless, the relative EPR signal intensities for the several  $g$ -limbs indicate that  $P_{bu}$  centers are not situated on faces of any one predominant orientation; i. e., the LPSi structure is not dominated by platelets or needles.

Despite qualitative similarities in thermochemistry, the progressive behavior of  $P_{bu}$  under thermal oxidation differs from  $P_{b0}$ . For  $P_{b0}$ , the  $g$ -values and linewidth ( $\Delta$ ) anisot-

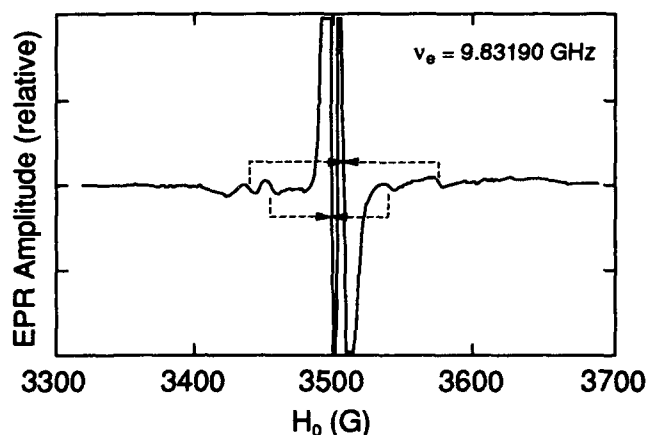


Fig. 1. EPR spectrum of luminescent porous silicon at 295 K, magnetic field parallel to a [110] axis, showing two sets of hyperfine lines, referenced to the pertinent central line by arrow markers.

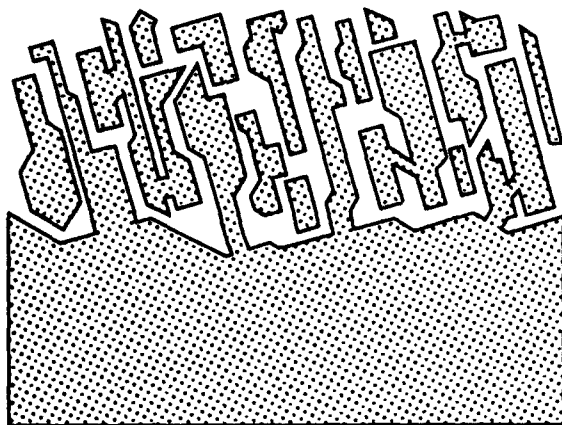


Fig. 2. Schematic structural model of porous Si, on a wafer substrate of unspecified and non-standard orientation, as suggested by EPR.

ropy ( $\Delta_{\parallel} = 2$  G,  $\Delta_{\perp} = 3$  G) barely change under oxidation. In strong contrast, for  $P_{bu}$  after gentle oxidation at 300 C,  $g_{\perp} \approx 2.005-2.006$  and  $\Delta_{\perp} \approx 10$  G. This indicates a significant change in the mean geometry of the  $P_{bu}$  center and its immediate surroundings, and a much greater site-to-site variation than occurs on a planar surface.

In all our tests, only the  $P_{b0}$  variety ( $\cdot\text{Si}=\text{Si}_3$ ) of  $P_b$  was seen; this is the only  $P_b$  defect observed on (111) or (110) wafer surfaces. The  $P_{b1}$  center (presumably  $\cdot\text{Si}=\text{Si}_2\text{O}$ ) of oxidized (100) wafers was not detected. On bare, etched wafers,  $P_{b0}$  centers reappear consistently, though  $[P_{b0}]$  is not necessarily monotonic. The  $P_{b1}$  center, however, often does not reappear at all

during native oxidation; and its relative concentration is highly dependent on chemical aspects of any subsequent thermal oxidation process.

The ascribed role of  $P_{bu}$  as a parallel non-radiative recombination route, competing with the unassigned luminescent center, was checked by successive oxidation and hydrogen anneal. The  $[P_{bu}]$  was increased by roughly a factor of 10 during oxidation, while luminescent intensity under a UV lamp declined from very bright to the naked eye to invisible, leading one to believe that  $P_{bu}$  may well be the dominant competing pathway. However, subsequent anneal in  $\text{H}_2$  reduced  $[P_{bu}]$  to its initial pre-oxidation value; but the luminescence did not recover to anywhere near the original intensity. Another sample showed greater recovery. Although  $P_{bu}$  is clearly a very important lifetime killer, other recombination centers seem to be present in variable quantity. One possibility is a second paramagnetic defect, not discussed here, which has an isotropic  $g$ -value of about 2.004–2.005, resembling defects known in bulk Si or  $\text{SiO}_2$ . Another possibility is the unassigned “ $P_{b2}$ ” center, which shows up via spin-dependent recombination (SDR) on the (100) wafer surface, but is invisible to normal EPR. Pertinently,  $P_{b0}$  is visible via SDR in all orientations on (111) Si, and on (100); but  $P_{b1}$  does not appear by SDR. Additional, quantitative study is needed to isolate and clarify the recombination mechanisms in LPSi (and the mysteries of the  $P_{b1}$  and  $P_{b2}$  centers on wafer surfaces).

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## ANISOTROPIC INTRARED-UP-CONVERSION LUMINESCENCE AND EXCITON DYNAMICS IN LIGHT-EMITTING POROUS SILICON

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We demonstrated for the first time that a porous silicon (PS) layer, which has a bright-emission in the range of 500-700 nm, exhibits a strong visible-range luminescence under the illumination of an infrared ultra short pulse laser (1.06  $\mu\text{m}$  of a passively mode-locked YAG laser)[1]. The infrared-up-conversion luminescence spectrum coincides exactly with the luminescence spectrum excited by the ultra-violet light, with the efficiency of former about three orders of magnitude smaller than that of the later. The dependence of up-conversion luminescence intensity on pump power verifies that it is a third-order nonlinear optical process. The third-order nonlinear optical susceptibility  $\chi^{(3)}$  of PS has a 2 order of magnitude enhancement relative to Si. The signal of the enhanced third harmonic generation in PS could act as an internal pump source to excite light emission just as the UV light does. The above results give a strong support to the quantum confinement mechanism of visible light emission from PS, as shown by previous work [2-4] that the nonlinear optical polarizability may be greatly enhanced for an assembly of multiple-quantum-well structures and semiconductor micro crystallites, which have one and three-dimensional confinement structures, respectively.

By using a linearly polarized incident light, it is found that the up-conversion luminescence signal intensity is anisotropic as the polarization vector of normally incident fundamental light is rotated with respect to the crystalline orientation.[5] The intensity vs rotation angle curve shows a fourfold symmetry, which is the same as that observed from Si single crystal, but the phase difference is  $180^\circ$  as compared with the curve of c-Si. It has been known[6] that if silicon is changed from crystalline Si to non-crystalline Si, the only difference between the curves of intensity-orientation is the reduction of modulation depth rather than the change of phase. For amorphous Si ( $\alpha$ -Si), the modulation depth should be zero. Therefore, our result gives an evidence that the a-Si is unlikely the possible mechanism of visible light emission from PS as suggested by Vasques et al. [7] On the other hand, the phase difference  $180^\circ$  implies that although the crystalline anisotropy is still remained in PS, but the microscopic property of PS is greatly different from that of c-Si due to the nanoscale structures.

The exciton dynamics in light-emitting PS is studied by using the temperature-dependent and picosecond time-resolved luminescence spectroscopy.[8] Two

luminescence bands centered at the wave-lengths of 610 nm and 700 nm (denoted as band E and S) are observed at 100 psec after the light excitation. The higher energy state (band E) dominates at the temperature below 200K, and does not contribute to the ordinary room temperature PL spectrum. We attribute the band E to the emission from confined exciton states in nanostructures of PS, according to its temperature dependence of luminescence intensity. As to the band S, which dominates at the temperature above 200K, we suggest it is most possibly originated from surface related localization states. The intensity decay of band E follows a nonexponential process described by two life-times. The incident light induces interband transitions and generates excitons in the quantum confined structures. There are two channels for the confined excitons to radiatively relax to the ground state. One is the direct recombination of electron-hole pairs, which dominates at low temperature with a de-excitation lifetime of about 3ns. Another channel is the coupling between confined exciton states (E) and localized states (S) through a thermal activation process at higher temperatures followed by a deexcitation transition from S to the ground state. The above suggested dynamic process provides an unified model which takes into account of both the quantum confinement effect and the surface related mechanism, and coincides conceptionally with the "kidney" model [9] proposed recently. Our picosecond time-resolved luminescence measurements also identify for the first time the confined excitons induced by the quantum size effect of PS, which has not been directly observed in previous experiments.

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## I-V CHARACTERISTICS OF POROUS SILICON - AN OBSERVATION OF PHOTOCONDUCTIVITY

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In order to avoid the metal/porous-Si contact problem and to study the electrical conduction of porous Si at a lower bias, transverse I-V characteristics were measured on the porous Si layer which was prepared in the p-type region of a shallow p/n junction by using conventional planar fabrication technique and electrochemical etching method. The p/n junction was made by low energy ion implantation on an n-type substrate with a resistivity of about  $3 \Omega\text{cm}$ . The junction depth was about  $0.4 \mu\text{m}$  and the boron concentration in the p-type region was of  $10^{19} \text{cm}^{-3}$ . After the deposition and the patterning of metal contacts on c-Si surface, porous Si was formed in the region between the two contacts with the etching direction being perpendicular to the junction. Anodization etching was conducted in 35% HF solution with short etching time ranging from 30 seconds to 3 minutes. Due to the presence of the p/n junction, the etching current density was low (10 mA over 2-inch wafer) and the maximum etching depth was limited by the junction depth. Cross-sectional TEM was used to examine the porous Si layer and images consistent with the preparation conditions were obtained. X-ray diffraction experiment showed the existence of c-Si grains in the porous Si layer.

When measuring the I-V characteristics, the current flowing in the porous Si layer of thus prepared structure is perpendicular to the etching direction. For samples with longer etching time, the etching depths are closer to the junction depth and the measured current levels are also lower. With etching time exceeding 1 minute, the etching depth can reach the junction depth, as revealed by XTEM. The measured resistivities of the samples with long etching times ranged between  $10^5 - 10^6 \Omega\text{cm}$  at room temperature and about  $10^{11} \Omega\text{cm}$  at liquid helium temperature. The Leakage current across the p/n junction was checked to be much smaller than the current in the p-type layer for all the samples under the bias condition we applied (under 5 V). The measured I-V curves showed weak nonlinearity which may be due to the c-Si/porous-Si interfaces. While the substrate leakage currents were very small but smooth, the porous Si I-V curves exhibited observable vibrations. One of our original motives for measuring transverse I-V was to see whether any resonant behavior exists. In our present samples, the distance between contacts is too large ( $500 \mu\text{m}$ ), so they cannot be used for this purpose. But the observed irregular vibrations might contain information about



the disorder and the interconnection of porous Si structure as well as about the conduction mechanism in the material.

By applying light onto the samples during the I-V measurement, we observed both photoconductive and photovoltaic effects. In the dark, the I-V curves pass through the origin. With a DC light source focused on the middle of the porous Si region, the curves still pass through the origin but the conductivity increases with increasing light intensity. Our reference sample without etching did not show this behavior. By varying the position of the light spot in the porous Si region, continuous varying photovoltage was observed. This might be due to the possible weak barriers at c-Si/porous-Si interfaces. The influence of parasitic p/n junctions on these two effects can not be excluded. Structures with deeper junctions and smaller porous Si regions are being fabricated to exclude the disturbance of the p/n junctions. Quantitative studies are also being proceeded to clarify the origins of the two effects.

The advantages of our lateral electrical conduction approach are manyfold: The Schottky-type barriers at the usual metal/porous-Si contacts are deleted. One only has to deal with the much weaker barriers at the c-Si/porous-Si junctions, so a better environment for studying the intrinsic electrical properties of porous Si can be obtained. And the possible reach-through problem during depositing metal layers on top of porous Si can also be avoided. Lateral devices are easily derived. Further electrical studies on porous Si, such as *mobility and carrier concentration measurements*, can easily utilize the generalization of our approach. All the fabrication processes are simple and inexpensive, consistent with the merits of porous Si.

### III. NANOSCALE SILICON - THEORY

## Abstract

International Workshop on Light Emission and Electronic Properties of Nanoscale Silicon  
UNC, Charlotte, February 1 - 3, 1993

### Electronic and Optical Properties of Nanoscale Silicon: Theoretical Issues

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Novel electronic and optical properties are found in silicon with nanoscale dimension perturbations e.g. short period Si/Ge superlattice structures, Si crystallites or porous Si. In particular, quantum size effects can influence the radiative properties. Recent observations of strong photoluminescence in porous Si samples has renewed considerable interest in this area.

Bulk Si has an indirect band gap with the conduction band edge states falling in six equivalent valleys near the zone faces along x, y and z. The valence band edge states are formed of the usual three fold p-like states, split by a small spin-orbit interaction. Superlattice periodicity or the boundary of a crystallite alters the translational symmetry. The band gap can become nominally direct, with dipole allowed transitions at threshold, due to the broken symmetry. This has been analyzed for the case of Si nanocrystallites within a simple envelope function approach [1]. The new dipole allowed transitions exhibit a radiative rate that is strongly size dependent with radiative times in the microsecond range for blue shifts of order 1 eV. This is in rough agreement with luminescence decay times observed in porous Si samples at room temperature.

A microscopic theory, based on local density calculations, has been done for H terminated Si wires of small cross section ( $\approx 10$  Å) [2]. Although rather small, they reveal interesting features which should carry over to larger, less symmetric structures. The multi-valley structure of the bulk conduction band edge states leads to a family of low lying states in the wires. The nominally degenerate valleys are split by a valley orbit interaction which yields both "fast" and "slow" dipole allowed transitions with the slow component being lower in energy. This could be a natural explanation for the observed long time component in the photoluminescence from porous Si at low temperatures.

The key theoretical issues at this time are (i) a careful consideration of the valley orbit splitting of the conduction band states together with the exchange splitting of the exciton for nanocrystallites; and (ii) the role of phonon assisted transitions in the radiative properties. Gross estimates [1] have already emphasized that phonon assisted transitions are quite competitive with confinement induced direct transitions for nanoscale Si particles. Recent experiments exhibit clear signatures of phonon assisted transitions. The exchange splitting of the exciton (together with the weak spin-orbit splitting) has been proposed to explain the fast and slow radiative components. Both valley orbit and exchange splitting are intrinsic features of the electronic states in Si nanostructures. A more detailed analysis will be required to sort them out and understand the relevance to observations.

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## EXCITONS AND DONORS IN QUANTUM DOTS \*

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Exciton recombination and binding energies and donor binding energy are among the crucial parameters that control optical and electronic properties of a system. Calculation of these parameters in the case of quantum dots embedded in an infinite matrix is more complicated than in the bulk because effects of the induced polarization at the dot-matrix interface must be included. The previous calculation of one- and two-electron ground state energies in quantum dot systems clearly indicates the importance of the polarization terms which must be included in the Hamiltonian since the use of a voltage-independent capacitance for their description does not offer a clear physical insight.

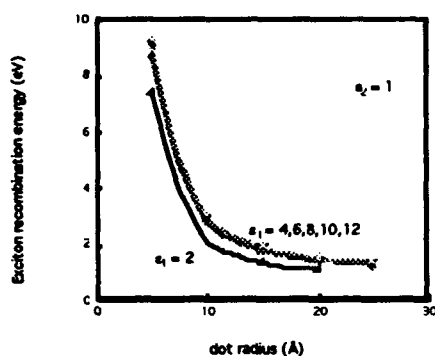
Exciton binding and recombination energies in a silicon quantum dot embedded in an infinite matrix such as silicon dioxide or vacuum are calculated as functions of dot size. Electron and hole are treated as independent particles within the effective mass approximation. Electrostatic effects, such as electron-hole attraction and induced mutual and self-polarization are included by perturbation. This approach is valid for small quantum dots where kinetic energy clearly dominates. Calculations are carried out for different values of both the dot's and matrix's dielectric constants in the range from 1 to 12 for the dot and from 1 to 4 for the infinite matrix. Reduction of the dot's dielectric constant for small quantum dots is accounted for by the modified Penn's model. The exciton binding energy is virtually independent of the dielectric constant of the infinite matrix. The exciton recombination energy increases only weakly with the dot's dielectric constant because of the *partial cancellation* of Coulomb and polarization terms. Figure 1 shows exciton recombination energy as a function of dot radius for different dielectric constants of both the dot and the infinite matrix. The exciton recombination energy is 1.92 eV and its binding energy is 130 meV for a 3 nm silicon dot embedded in vacuum whose dielectric constant is 8.18, according to the modified Penn's model. This compares well with the luminescence peak observed in porous silicon which varies from 1.6 to 2 eV and the measured exciton binding energy of 100 to 120 meV. Detailed plots of the exciton binding and recombination energies are presented in Figure 2.

The ground state energy of an electron in a quantum dot with a singly ionized donor impurity at the center of the dot is calculated by the variational method within the effective mass approximation. The energy of the lowest quantum confined state above the conduction band edge is estimated by treating the electrostatic energy as a perturbation. An electron in this state capable of resonantly tunneling to the other dots may be considered free to propagate through the system. The binding energy of a donor impurity in a quantum dot is thus the difference between this lowest quantum confined state and the impurity's ground state. This is to be contrasted with the binding energy in the bulk where an electron is excited to the conduction band edge only. Therefore, the binding energy, as we defined it, depends on the dielectric constant of the quantum dot. The modified Penn's model is used to account for the reduction in the static dielectric constant, which is then incorporated into our calculations for the donor's ground state and the lowest quantum confined state. Figure 3 shows calculated donor binding and ground state energies with and without polarization effects. The donor binding energy for small quantum dots is much larger than in the bulk. For very large dots it approaches the bulk donor limit corrected for polarization effects. Inclusion of the polarization effects increases the donor binding energy by about factor of 3.

The results of this work confirm the paramount importance of the polarization effects for the correct description of the physics of quantum dots. The characteristic energies of excitons and donors in quantum dots are notably different than the corresponding bulk values. Conventional bulk solid approach must be therefore substantially modified when applied to quantum dots.

\* Supported by ARO and ONR

Exciton energy - different dielectric constants of the dot



Exciton energy - different dielectric constants of the matrix

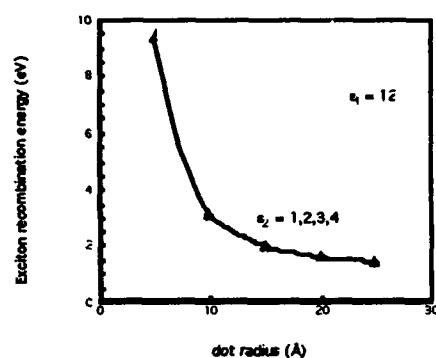
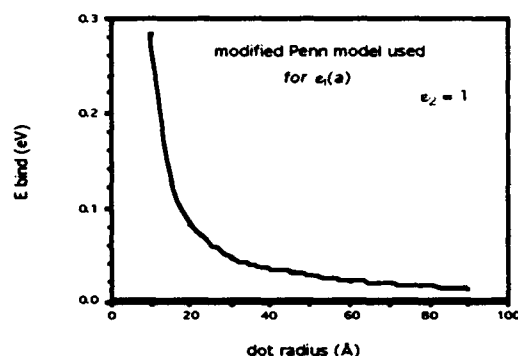


Fig 1. Exciton recombination energy as a function of dot radius for different dielectric constants of dot  $\epsilon_1$  and matrix  $\epsilon_2$ .

Exciton binding energy



Exciton recombination energy

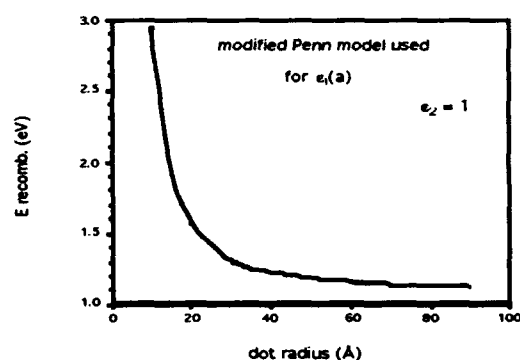
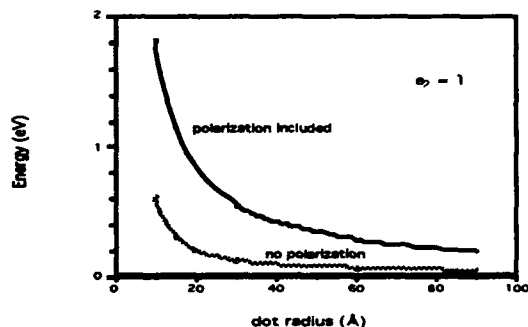


Fig 2. Exciton binding and recombination energy for a silicon dot whose dielectric constant is described by the modified Penn model.

Donor binding energy



Donor ground state energy

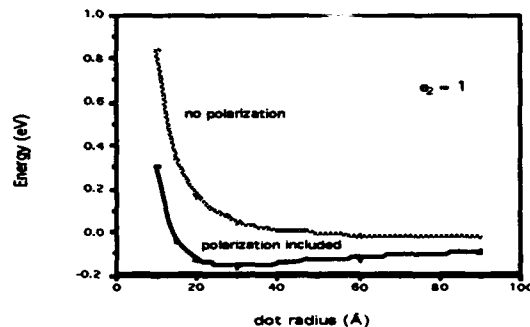


Fig 3. Donor binding and ground state energies as functions of the silicon dot radius with and without polarization effects.

# THEORY OF ELECTRONIC, OPTICAL AND TRANSPORT PROPERTIES IN SILICON QUANTUM WIRES

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Recent observation of efficient luminescence in porous silicon has stimulated interest in the electronic and optical properties of Si quantum wires which are believed to be present in porous silicon samples under very specific fabrication conditions [1]. We present theoretical studies of electronic, optical and transport properties of ideal silicon quantum wires. The ideal wires are oriented along (001) with a square cross-section whose faces, of width  $L$ , are parallel to the four equivalent (110) planes. Silicon dangling bonds at the surface are passivated by hydrogen. The electronic and optical properties are treated in a second-neighbor empirical tight-binding model with excitonic effects included in the effective mass approximation [2,3]. Carrier transport is treated in a Boltzmann transport framework with nonpolar deformation potential acoustic phonon scattering being the dominant scattering mechanism [4].

## Absorption Coefficient

Absorption coefficient vs. photon energy for 7.7 and 15.4 Å quantum wires is shown in Figure 1. The solid curves correspond to plane polarized light with the electric field oriented along [110] or  $\bar{1}\bar{1}0$  (x-polarization) while the dotted curves correspond to light polarized along

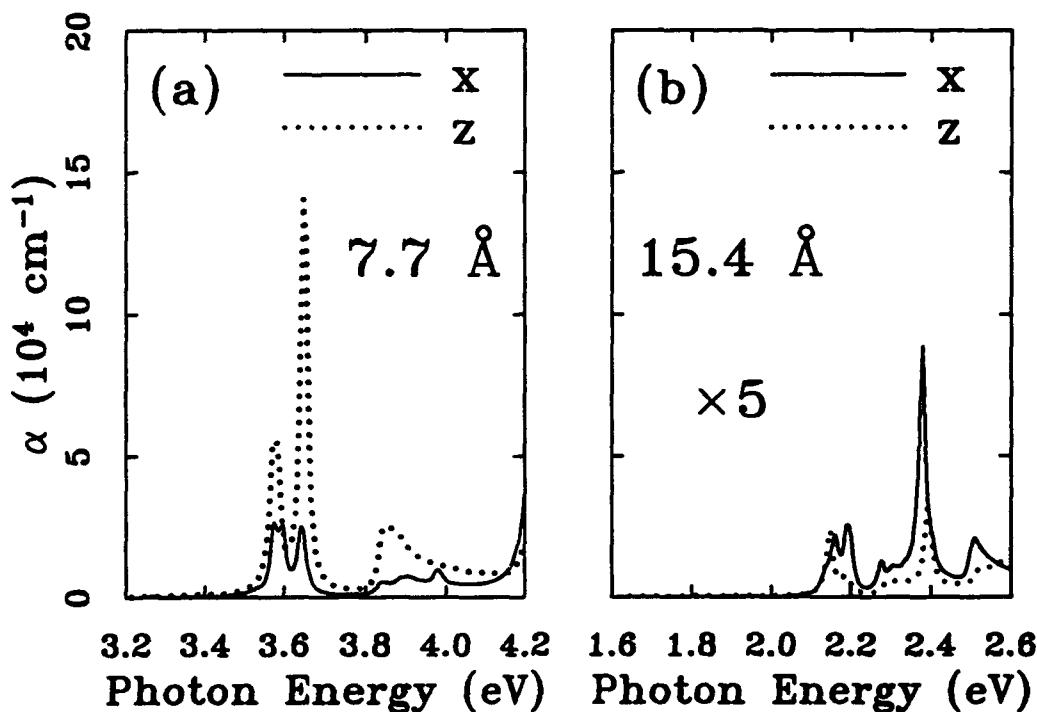


Figure 1. Absorption spectra for Silicon quantum wires with widths of (a) 7.7 and (b) 15.4 Å. The solid curve is for x-polarization and the dotted curve is for z-polarization. The absorption spectrum is dominated by excitonic effects. Note the rapid decrease in absorption strength with wire size.

[001] (z-polarization). The spectra are broadened with a Lorentzian half width of 0.01 eV. The absorption is anisotropic and dominated by excitonic effects. The exciton oscillator strengths decrease slightly faster than  $1/L^5$  [2,3].

### Electron Mobility

Low field electron mobilities at 300 K are shown in Figure 2 for wire widths between 7.7 and 23 Å. The mobilities depend on wire size and vanish as  $L \rightarrow 0$ . Relaxation time estimates for electron mobilities are indicated in Figure 2, in fair agreement with the Monte-Carlo results. Mobilities in narrow silicon quantum wires are low in comparison with bulk silicon [4].

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### ACKNOWLEDGMENTS

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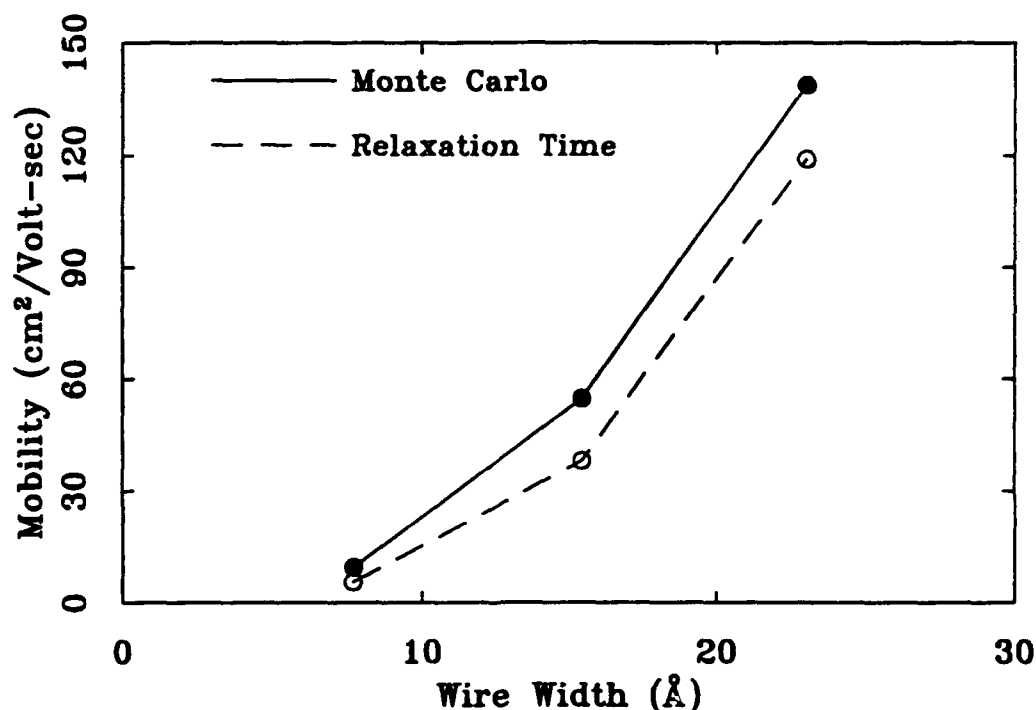


Figure 2. Low field mobilities as functions of wire size at 300 K for electrons (solid curve) in silicon quantum wires from Monte Carlo simulation. A simple relaxation-time estimate for the electron mobility (dashed curve) is shown for comparison.

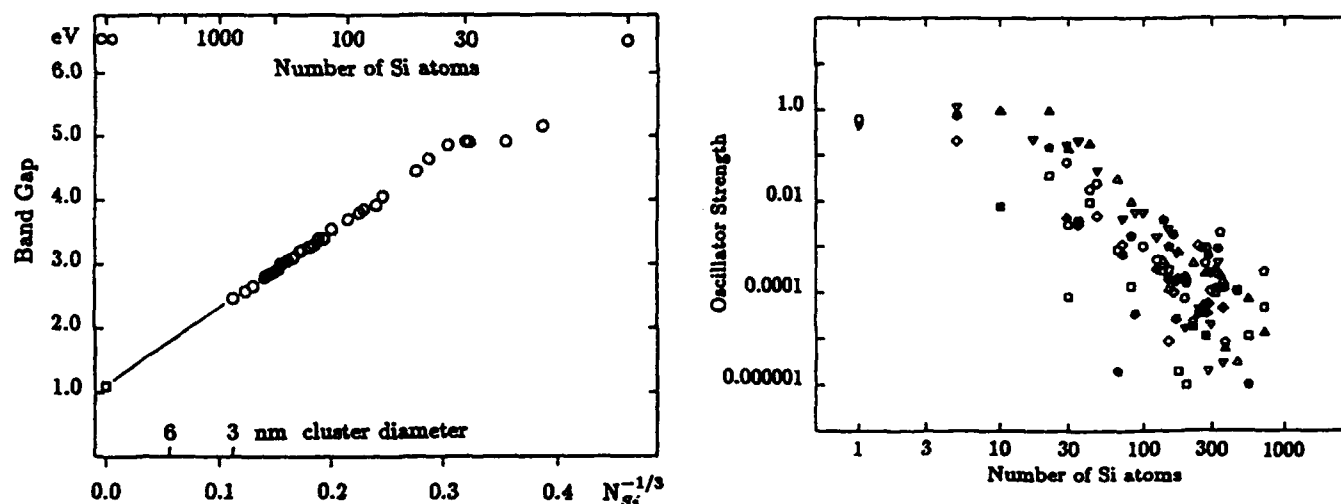
# DENSITY FUNCTIONAL THEORY AND QUANTUM EFFICIENCY OF NANOSTRUCTURED SEMICONDUCTORS

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*Nanostructured semiconductors show unusual material properties like strong visible luminescence for materials with an indirect gap like silicon and germanium. It is found from first principles calculations on realistic size particles that such effects originate intrinsically from quantum confinement. Finally, the quantum efficiency of measured photoluminescence data is discussed.*

Nanostructured materials can show dramatically modified properties as compared to the corresponding bulk materials. The discovery of strong visible luminescence in nanostructured Si and Ge is a striking example of a qualitative change in materials properties. A hot debate has followed the discovery whether the effect is due to quantum confinement or whether it is rather due to compounds typically adsorbed at the surface. We have decided to discuss this question at a theoretical level. It is desirable for a non prejudiced theoretical study of the phenomenon to not rely on a parametrization of materials properties in either the bulk or the cluster domain. Provided that first principles studies are feasible for nanostructured materials they would be preferable to calculations using parametrized material properties. In fact with recently developed computational possibilities [1],[2] it is feasible to study the confinement effect for high symmetry clusters of realistic size.

First principles density functional studies have been done for hydrogen passivated Si clusters exceeding one thousand atoms in size [3],[4],[5]. It is expected that intrinsic properties of real lower symmetry clusters are evidenced already in the idealized high symmetry clusters. The two types of cluster with  $T_d$  symmetry, namely the one with a tetrahedral interstitial at the origin and the one with an atom at the origin, yield exactly the same linear scaling of the bandgap with the inverse cluster diameter. This is shown in Fig. 1. Other density functional calculations [6],[7] for quantum wires (rather than dots) give also a linear function of the gap versus inverse diameter with about half the slope valid for dots shown in Fig. 1.



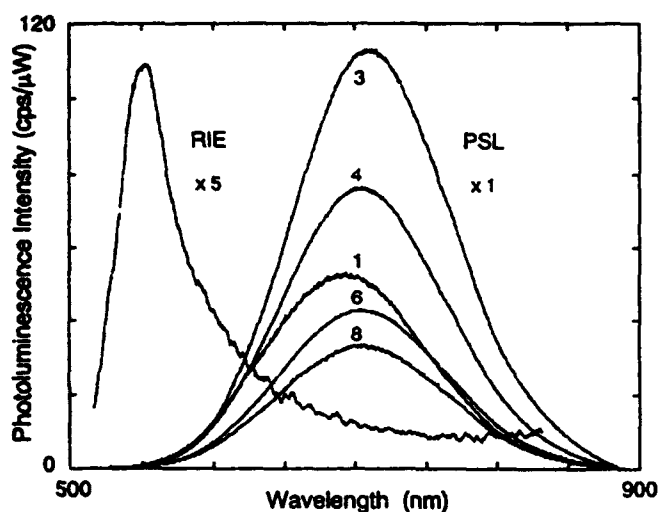
The calculated energy gaps, ranging from 1.5 eV to 2.5 eV for particles in the diameter range of 10 nm to 3 nm, are consistent with experimental size estimates for nanostructured Si and observed luminescence spectra. It is also interesting to note that semiempirical  $k \cdot p$  estimates based on the bulk effective mass of the bandgap for isolated nano-clusters would yield a quadratic rise of the bandgap with



inverse diameter in qualitative discrepancy with the first principles study, the discrepancy arising from the unjustified neglect of electrostatics for free quantum dots by the basic  $k \cdot p$  model.

Self-energy corrections are known to be of importance for the exact determination of the energy gap in bulk silicon. We have found that a size independent self-energy correction is adequate down to the tetrahedral neo-pentasilane molecule where optical absorption measurements are available.

Optical transitions between the valence band top and the conduction band bottom are allowed in clusters of sufficiently low symmetry. In the bulk limit the transition is indirect and thus forbidden except for the symmetry breaking through the phonons. The present calculations for finite clusters are entirely consistent with such expectations. Fig. 2. shows the oscillator strength as a function of the number of Si atoms in the cluster. The oscillator strength is near one for the smallest clusters and approaches zero for very large clusters.



As a point of general interest the question of quantum efficiency of photoluminescence results should be dealt with. When comparing the results of different origins, it appears to be useful to be able to judge the absolute efficiencies of photoluminescence results. Referring to the results [4] shown in Fig. 3, the photoluminescence intensity is given in photoelectron counts per sec. Given the exciting laser light of 1 mWatt at 488 nm, focussed to a spot of 30  $\mu\text{m}$ , an instrumental width of 0.13 nm, a photoluminescence collection under 0.28 sr, and an instrumental efficiency (spectrometers and GaAs photomultiplier, including mirrors and lenses) of about 0.008, all the requirements are now available for calculating the spectral quantum efficiency (differential per nm and sr), which in this case amounts to about

$1.6 \times 10^{-7} \text{ nm}^{-1} \text{ sr}^{-1}$ . The integral quantum efficiency, integrated over curve 3 in Fig. 3, and the spatial angle, would amount to an order of magnitude of about 0.1 %. In other cases an up to four times higher value was observed. It is proposed that in future work, instead of using uncomparable 'arbitrary' units one should include all the necessary factors in publishing intensities, to allow at least an order of magnitude comparison with other work.

The authors gratefully acknowledge the fruitful collaboration of H.Auderset in the experimental part of this work.

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#### IV. TRANSPORT IN NANO-PARTICLES

## SEMICONDUCTOR QUANTUM DOT RESONANT TUNNELING SPECTROSCOPY

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Carrier confinement to reduced dimensions has led to numerous important developments in basic semiconductor physics and device technology. Until recently, this confinement has only been realizable by an interface and thus the confinement is only in one dimension. Though the technology to create lateral confining potentials is considerably less advanced than the degree of control that exists in the vertical epitaxial dimension, remarkable progress has been made in imposing quantum confinement in additional dimensions. Recently, 3-dimensionally laterally-confined semiconductor quantum wells ("quantum dots") have been realized. These structures are analogous to semiconductor atoms, with energy level separation of order 25 meV, and tunable by the confining potentials. A systematic study reveals a (radius)<sup>-1</sup> dependence on the energy separation. The electronic transport through quantum dots will be presented and analyzed. The spectra corresponds to resonant tunneling from laterally-confined emitter contact subbands through the discrete 3-dimensionally confined quantum dot states. Momentum selection rules will be discussed, and it is found that non-conservation is observed in these structures. Results on coupled quantum dot states, on the amount of inelastic scattering, and a discussion of coincident Coulomb blockade will be presented.

## Electron Transport in Nanoscale Silicon Embedded in Amorphous SiO<sub>2</sub>

by

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Three dimensional quantum confinement can be observed at room temperature in a lattice mismatched heterojunction provided the potential well in the double barrier layer is sufficiently deep, and the particle size small. Under these conditions, the large separation of energy levels results in negligible electron-phonon interaction that can destroy coherence. By satisfying these conditions, three dimensional quantum confinement has been observed at room temperature<sup>(1)</sup> in a double barrier structure consisting of a layer of silicon microcrystallites embedded in an a-SiO<sub>2</sub> matrix sandwiched between an aluminum contact, and an n-type c-Si substrate. This structure is fabricated in an inexpensive e-beam evaporator operating at a modest vacuum pressure. Figure 1 shows the equivalent parallel conductance ( $dI/dV$ ) measured at 1 MHz, and dc current as functions of applied bias for this structure. These curves, measured at room temperature, are reproducible after any number of bias sweeps either from low to high or high to low negative bias. The sharp conductance peaks suggest that all the quantum dots are nearly the same size possibly because surface tension and oxidation favor the formation of spherical microcrystallites all the same diameter as the film thickness. Between each resonance in Fig. 1 indicated by a current step, the current increases monotonically with increasingly negative bias because the Fermi sphere in the aluminum is large. The lattice mismatched Si-SiO<sub>2</sub> heterojunction has a large density of localized electron states located in both the silicon microcrystallite and substrate surfaces. Quantum confinement widens the fundamental energy gap exposing more localized electron states. The understanding of our original model<sup>(1)</sup> of transport is extended to include electron trapping in these states. The states below the Fermi level in the aluminum, which controls the occupancy of these states, are full and charged. As a result, the I-V characteristics of the double barrier structure are dominated by coulomb blockade due to trapped charge. The electron states in the coulomb blockade model must included the coupled states of quantum confinement and localized states. The large voltage drop across the substrate depletion layer did not allow a clear picture of the role of quantum confinement and coulomb blockade in our previous work<sup>(1)</sup>. To overcome this problem, the equivalent circuit of the structure is obtained to determine the division of applied voltage between the double barrier and substrate depletion layers. Because of the large current flow at resonance, the parameters of the equivalent circuit have been obtained only prior to the onset of the first resonance. Figure 2 shows the dc equivalent circuit which was derived from ac measurements of the impedance and phase as functions of frequency from 20 kHz to 4 MHz, and the dc I-V characteristics both over an applied bias range from -5 to -10V as parameter. At dc, the applied bias divides between the double barrier and the substrate depletion layer according to the bias dependent values of  $R_Q$  and  $R_s$ , where  $R_Q$  represents the energy loss due to inelastic tunneling in the double barrier layer, and  $R_s$  represents the energy loss due to thermalization by scattering of hot electrons injected into the substrate from the double barrier. Figure 2 shows that the voltage across the double barrier layer is a few tenths of a volt, and becomes increasingly negative with increasingly negative applied bias.

The voltage separation between the first two conductance peaks in Fig. 1 is 0.25V and between the second and third it is 0.6V. Assuming that each microcrystallite is sandwiched symmetrically between the two oxide barriers, the energy separation in volts between the conductance peaks is half the difference in applied bias between the conductance peaks. Thus, the energy separation between the first and second peak in Fig. 1 is 0.13V, and between the second and third it is 0.3V.

The observation of quantum confinement at room temperature in a Si-SiO<sub>2</sub> heterojunction using inexpensive fabrication tools commonly used in silicon IC manufacture, and a relatively large energy separation between quantum states opens new possibilities of functional device applications.

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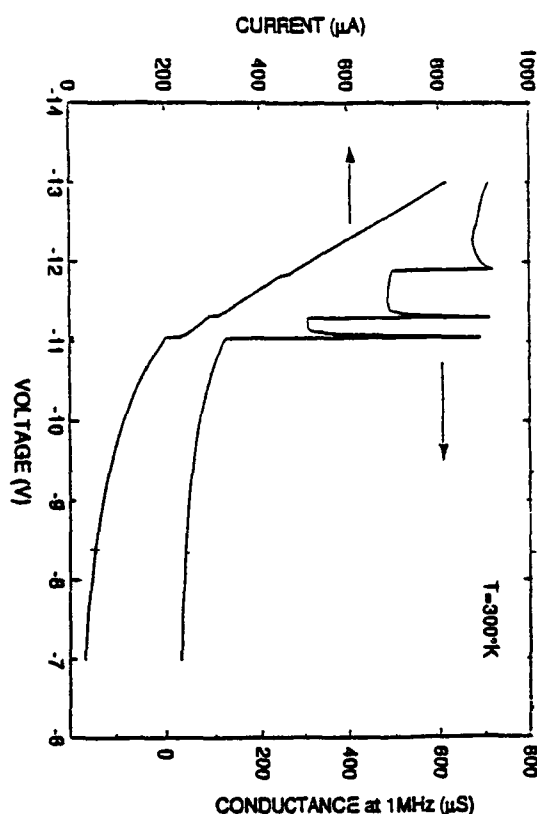


Fig.1 Reverse current and equivalent parallel conductance vs applied bias measured at a frequency of 1MHz and at room temperature (300K)

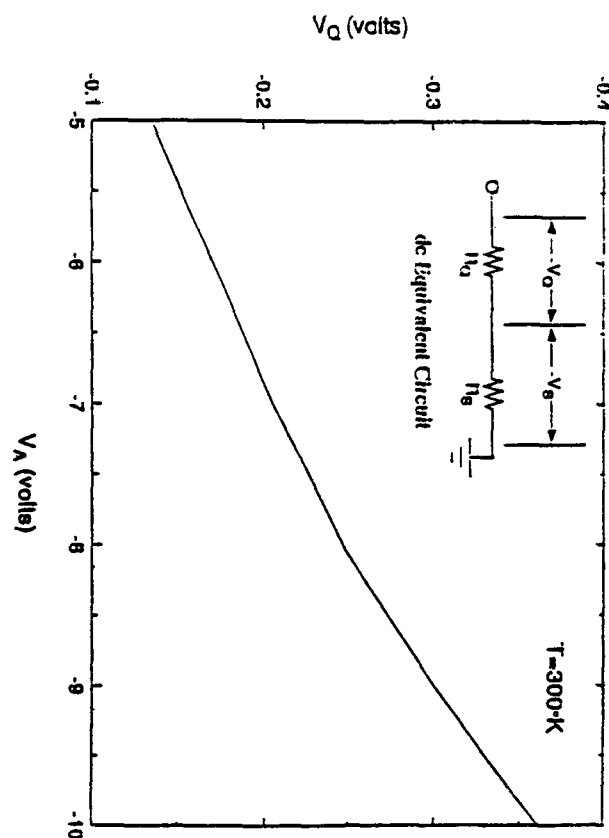


Fig.2 Voltage across the double barrier layer,  $-V_Q$ , vs applied Bias  $-V_A$ . The insert shows the dc equivalent circuit.

V. ELECTRO-LUMINESCENCE IN POROUS SILICON

## NANOSCALE DEVICE LESSONS LEARNED FROM POROUS SILICON

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Experiments at the Army Research Lab at Ft. Monmouth over the past year and a half provide a guide for our experiments in light emission devices using nanoscale silicon. The correlation of Raman and photoluminescence (PL) spectra was strong evidence for the PL originating in crystalline quantum confined Si structures with sizes on the order of 2-3 nm.<sup>1</sup> TEM studies showed that the porous silicon films were composed of regions of individual nanocrystallites in the interior of the porous Si film and a region of larger confined crystalline structures connected to the bulk Si at the interface.<sup>2</sup> The blue shift of the PL peak with hydrostatic pressure is opposite to the behavior of crystalline Si and indicates that the quantum confinement substantially alters the band structure in the nanocrystallites toward a pseudo-direct band gap.<sup>3</sup> The linear dependence of the PL with excitation power over many orders of magnitude demonstrated that the PL mechanism was a one photon-one electron process. The temperature dependence of the PL intensity and time delays was very similar to those reported by Hall and coworkers<sup>4</sup> for excitonic complexes in crystalline Si. The decrease in PL at higher temperatures exhibited a dissociation energy of about 100 meV, however the PL persisted to much higher temperature than in Hall's excitonic complexes.<sup>5,6</sup> Hall has pointed out that quantum confinement can cause the PL of bound excitons to persist to higher temperature than for bound excitons in the bulk crystal.<sup>7</sup> The increase in the PL time delay of one and a half orders of magnitude as the temperature was lowered from room temperature to 10<sup>0</sup> K (see fig. 1), as in Hall's experiments, suggests that a metastable bound excitonic state (with dipole forbidden transition to the ground excitonic state) is preferentially occupied at the lower temperatures<sup>4</sup>. Recently electroluminescence (EL) has been observed from two distinctly different regions within the porous silicon. A solid state LED was constructed with a very thin porous Si film (between 100 and 200 nm) in order to explore the effect of the Si structures at the Si-porous Si interface. EL with a faster delay time (less than 2 microseconds) and spectrum peaked at a longer wavelength (in the IR) is associated with a region of better electrical connectivity and larger structure sizes at the porous Si-crystalline Si interface. EL with a slower time delay (100-1000 microseconds) and with a spectrum peaked in the visible range is associated with a region of poor electrical connectivity within the porous Si film. Theoretical analysis shows that quantum confinement and surface polarization effects in the Si nanocrystallites produce a significant reduction the dielectric constant and result in large increases in binding energy of impurities and the prediction of electrical carrier freeze-out for common dopant impurities.<sup>8</sup> The temperature dependence of the faster EL component (see fig.2) appears to support this prediction. This effect may also play a role, along with freeze-out in traps or surface states, in the temperature dependence of the slower EL component (see fig. 3).<sup>9</sup>

These results indicate that the following rules of thumb may be useful in developing light emitting quantum-confinement device concepts:

- A. Device operation should be based on luminescent recombination of carriers in quantum confined Si structures.
- B. The quantum confined recombination region of the device will be mainly intrinsic due to the difficulty in doping.
- C. Electrical connectivity of both electrons and holes to the quantum confined structures must be maximized. Regions near an interface with crystalline Si may be favored.
- D. Deliberate introduction of isoelectronic impurity complexes into the quantum confined structures should be considered.

An example of a device structure utilizing these rules of thumb is shown in fig. 4. Silicon tips with nanoscale dimensions are formed on a P-type silicon substrate. The SiO<sub>2</sub> layer grown on the surface will grow thinner on the tip points due to their increased surface strain. An ITO (indium tin oxide) layer is used as a transparent N-type electrical contact. When a voltage is applied as shown, the E field enhancement at the tip points will

draw holes into the confined region. Electrons from the ITO will preferentially tunnel through the thinner oxide at the tips to recombine with the holes in the quantum confined region. Bound excitonic complexes can be formed in the tips by impurity implantation.

a. Work done while author was a National Research Council-ETDL associate.

b. GEO-Centers, Inc., Lake Hopatcong, NJ 07849.

c. Partial support from US Army Rsch. Off. and Off. of Naval Rsch.

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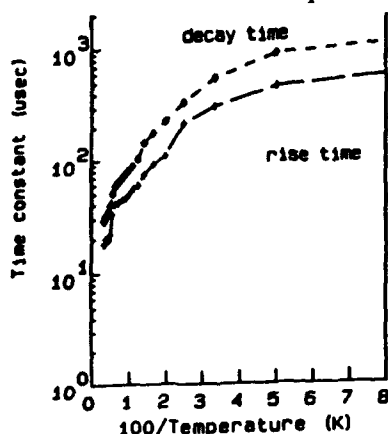


Fig. 1 Temperature dependence of PL time constants.

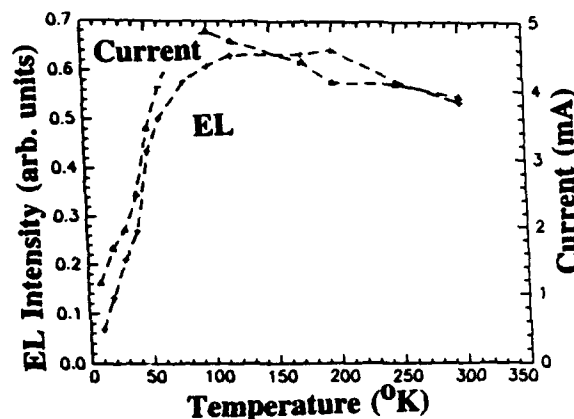


Fig. 2 Temperature dependence of faster EL.

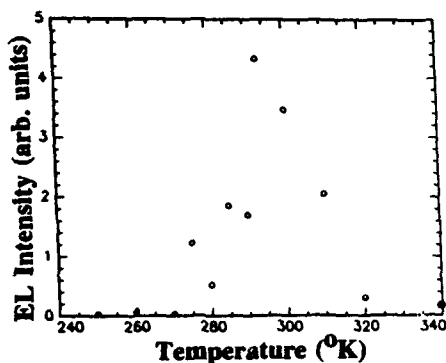


Fig. 3 Temperature dependence of slower EL.

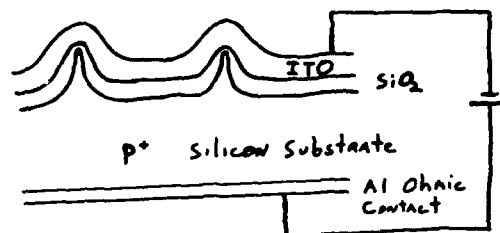


Fig. 4 Proposed quantum confined EL device structure.



# STUDY OF PHOTO- AND ELECTRO- LUMINESCENCE IN POROUS SILICON

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## Introduction

Strong luminescence in porous silicon is attracting interest in our group both from the point of view of the carrier dynamics and from the point of view of pn junction device fabrication. We review our recent work of photo- (picosecond luminescence decay measurements) and electro- ( $\mu\text{c-SiC}/\text{porous Si}/\text{crystal Si}$  pn junctions) luminescence in porous Si.

## Picosecond luminescence decay

The picosecond luminescence decay measurements were performed with the SH of cw modelocked YLF laser ( $\lambda = 527$  nm) and a synchroscan streak camera through a spectrometer. The pulse duration was 40 ps, the repetition rate 76 MHz and the excitation power density 100 mW/cm<sup>2</sup>. The time resolution of the synchroscan streak camera was 10 ps.

The picosecond luminescence decay becomes faster with increasing photochemical dissolution [1]. In particular, initial decay that has a single exponential component becomes faster at 520 ps for 0-min, 385 ps for 1-min, 240 ps for 3-min, and 110 ps for 5-min dissolution time. Figure 1 (a) and (b) show the picosecond time-resolved luminescence spectra for 1-min and 5-min dissolution time. Figure 1 (a) shows the rapid red shift of the luminescence peak from 600 nm to 620 nm within 500 ps. However, this red shift gradually disappears with increasing proportion of chemical dissolution as shown in Fig 1 (b).

On the basis of the structure for these samples measured by FTIR, TEM and Raman analysis, we consider that the excited carrier dynamics is subject to both charge transfer to surface states and recombination in Si microcrystal core states.

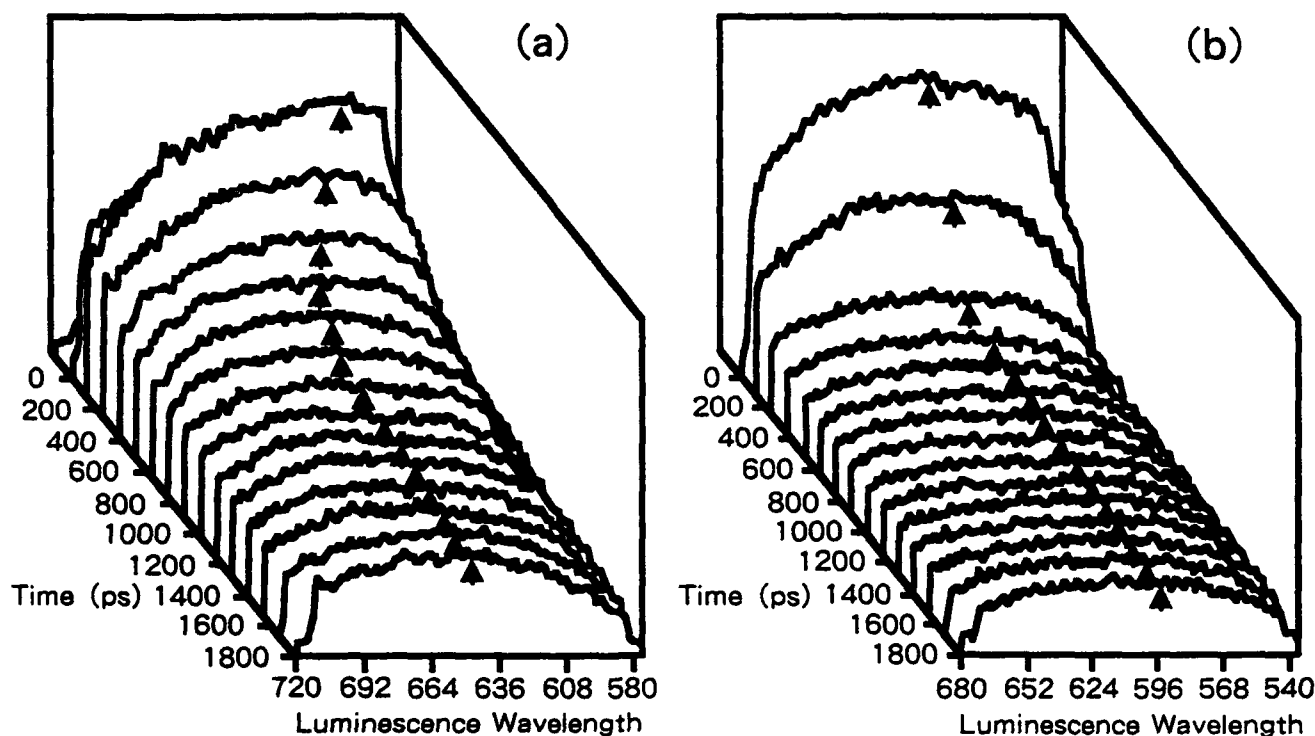


Figure 1. Picosecond time - resolved luminescence spectra for (a) 1 minute, and (b) 5 minute photochemically dissolved porous Si samples. Each spectrum is taken every 130 ps.

Chemical dissolution influences the hydrogen terminations on a Si microcrystal core that determine this charge transfer rate and changes the origin of the luminescence from surface states to quantum confinement states.

### Microcrystalline SiC/porous Si/crystal Si pn junctions

The structure of a  $\mu\text{c-SiC}/\text{porous Si}/\text{c-Si}$  pn junction diode is shown in Figure 2. The n-type  $\mu\text{c-SiC}$  was deposited on a porous Si layer (0.2–0.4  $\Omega\text{ cm}$ , 20  $\text{mA}/\text{cm}^2$ , 3 min) of thickness 150 Å using electron cyclotron resonance plasma chemical vapor deposition (ECR plasma CVD). The ECR plasma CVD conditions are as follows: a microwave power of 300 W, a deposition temperature of 300 °C, a gas pressure of 5 mmTorr, and a gas ratio of  $\text{SiH}_4:\text{CH}_4:\text{PH}_3:\text{H}_2 = 1:2:0.01:190$ . The optical band gap and dark conductivity of the  $\mu\text{c-SiC}$  used here were 2.3 eV and  $10^{-1}\text{ S}/\text{cm}$ , respectively [2]. In order to ensure that the porous Si layer was responsible for the luminescence, we confirmed that the  $\mu\text{c-SiC}$  film showed no photoluminescence at room temperature. After the deposition of the  $\mu\text{c-SiC}$ , ITO (600 Å thickness) was evaporated on 1- $\text{cm}^2$  area as a transparent electrode.

Figure 3 shows the current-voltage characteristics of this LED. Open and solid circles refer to the positive bias applied to the p-type c-Si substrate (forward direction) and the negative bias (reverse direction) respectively. The rectification ratio was about 100 at  $\pm 5\text{ V}$ . When the forward current density exceeded about 12  $\text{mA}/\text{cm}^2$  at 18 V, a uniform light emission from the whole ITO area could be observed with the naked eye. The light emission was stable, reproducible and showed no degradation over several hours. The electroluminescence spectrum is broad with a peak wavelength of 700 nm, similar to that of the photoluminescence spectrum. The luminescence intensity increased with increasing forward current density, whereas in the reverse direction no light emission was observed. These results suggest that the light emission is not due to electroluminescence of the intrinsic-type but of the injection-type [3].

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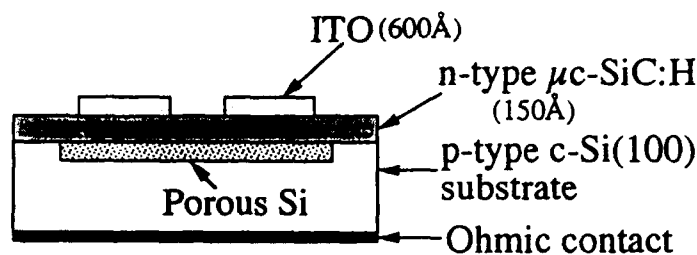


Figure 2. Structure of  $\mu\text{c-SiC}/\text{porous Si}/\text{c-Si}$  pn junction diode

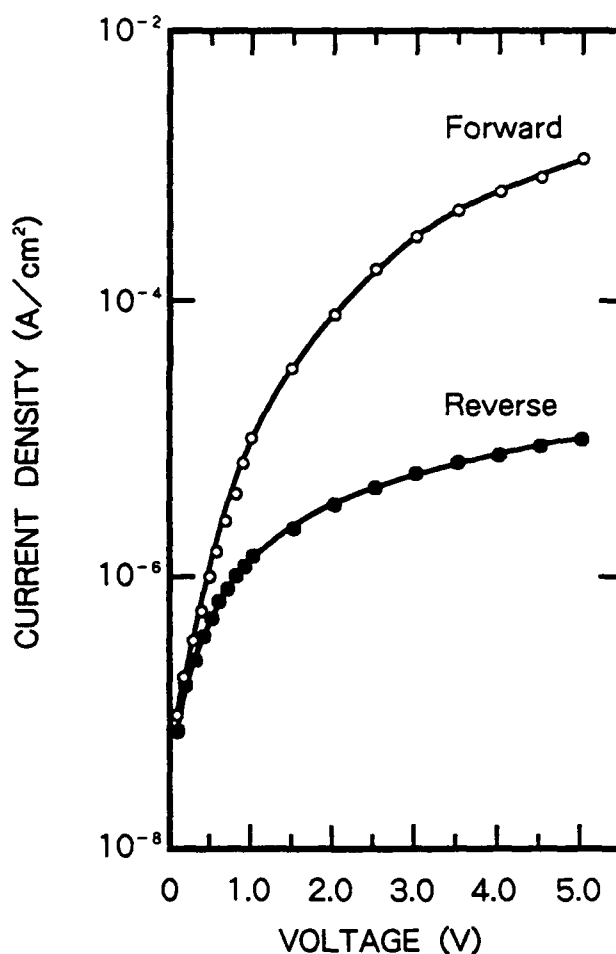
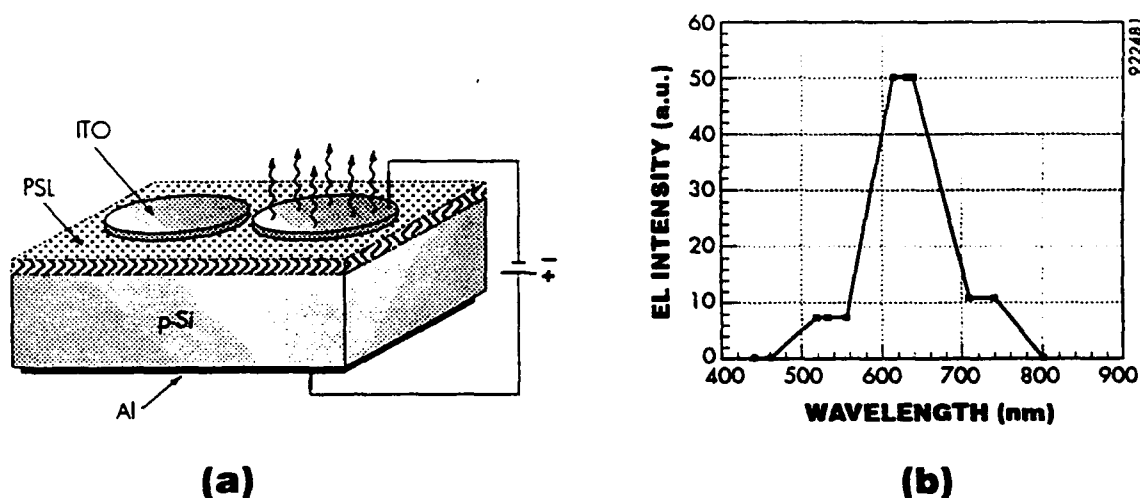


Figure 3. Current-voltage characteristics of the porous Si/ $\mu\text{c-SiC}$  LED.

# BRIGHT HOPES FOR EFFICIENT SILICON-BASED LIGHT-EMITTING DIODES

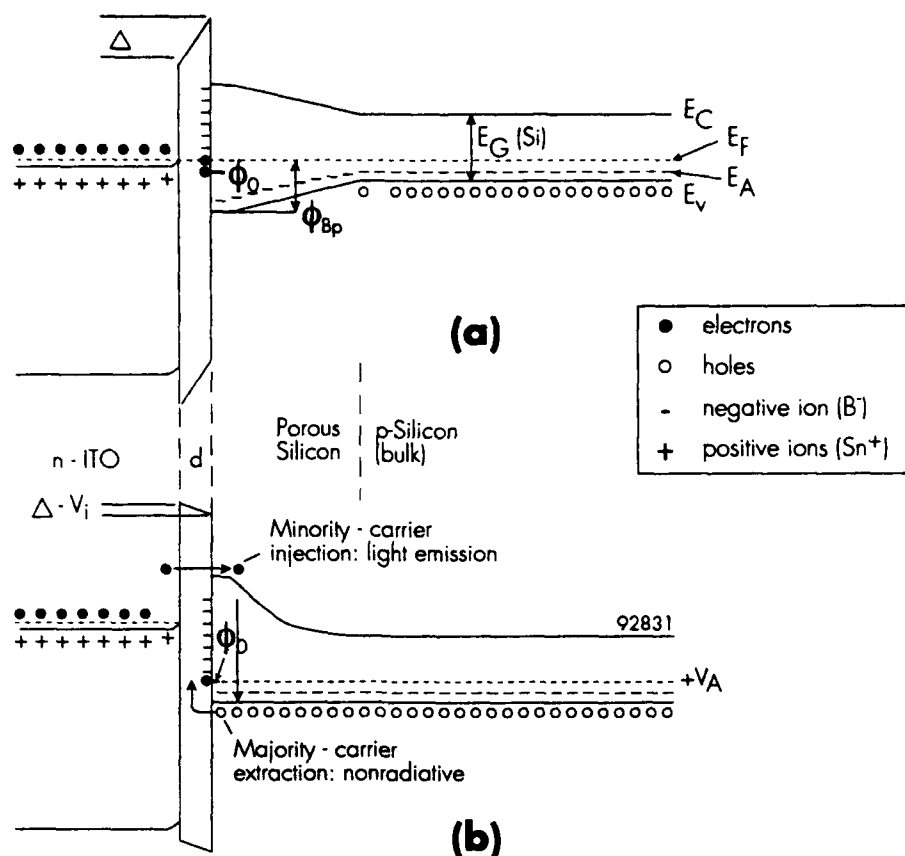
F. Namavar, N.M. Kalkhoran, and H.P. Maruska  
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We have demonstrated<sup>1,2,3</sup> the fabrication of heterojunction porous silicon visible light-emitting devices. Our device consists of a heterojunction between an electrochemically etched p-type porous silicon sample and indium-tin-oxide (ITO), a transparent n-type semiconductor which was deposited by RF sputtering. Figure 1 shows a schematic and measured electroluminescence (EL) spectrum of this device. Recently, our results were confirmed by other researchers.<sup>4</sup> We have carried out a further study to determine electrical properties and structural characteristics of these porous silicon/ITO structures. On the basis of three independent measurements, current-brightness,<sup>2</sup> current-voltage,<sup>1,3</sup> and current-temperature,<sup>5</sup> our results indicate that observed electroluminescence (EL) originates from minority (electron) carrier injection, the basic mechanism operating in GaAs-based LEDs or other homojunction devices. Figure 2 shows an energy band diagram model for ITO/porous silicon LEDs fabricated at Spire. Our finding indicates that EL should be possible with the same impressive efficiency levels as the photoluminescence (PL) which was observed for porous silicon. Furthermore, no physical or fundamental principles have been observed which would otherwise limit the efficiency of emissions of these devices. Lack of efficient EL in preliminary devices can only be attributed to the poor quality of the materials or the unoptimized processing.



**Figure 1** a) Schematic structure and b) EL spectrum of the porous silicon/ITO heterojunction LEDs.

The development of efficient, room temperature, silicon-based LEDs may allow implementation of practical optical interconnect technology for high speed chip-to-chip communication as well as the manufacture of low-cost, lightweight Si-based flat panel color displays for commercial and military computer monitors or television screens. The key to the success of the integration of porous Si-based devices with bulk Si electronic technology lies in the compatibility of fabrication processing. Hence, we have carried out experiments to evaluate the possibility of using conventional silicon photolithographic processing steps to pattern selected device regions both before and after the formation of porous silicon layers. Our results indicate that etch resolutions better than 5 microns<sup>6</sup> can be achieved using a multiple photoresist coating process for patterning. This approach reduces the probability of the existence of cracks or pinholes which can result in the etching



**Figure 2** *Proposed energy band diagram model for ITO/porous silicon heterojunction LEDs: a) in equilibrium and b) under forward bias.*

of undesired regions on the sample during the dynamic anodic etching in HF electrolyte. We have found that the etch resolution is strongly dependent on anodization conditions and can be improved by lowering the applied current density and shortening the etch period.

#### ACKNOWLEDGMENT:

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VI.

## NANOCRYSTALS

## Luminescent Direct and Indirect Gap Semiconductor Nanocrystals

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For about a decade there has been a systematic effort to understand the optical and structural properties of direct gap semiconductor crystallites that show three dimensional quantum confinement(1,2). In this work the quality and characterization of the samples is most important, as real samples have distributions of size, shape, and surface structure that introduce inhomogeneous averaging into the experimental properties. Perhaps some of the best characterized are nanometer CdSe crystallites made by organometallic chemical synthesis, and optically investigated at low temperature in an organic glass(3). The absorption spectrum is dominated by strong, discrete transitions due to three dimensional quantum confinement. Hole-burning and photoluminescence excitation spectra show that these transitions have substantial homogeneous as well as inhomogeneous widths. Detailed study of the time, wavelength, and polarization dependence of the isoenergetic "band edge" luminescence implies that the emitting state has an electron in an internal 1S state, and the hole on the crystallite surface in a disordered surface band. The states seen in absorption are interpreted as resonances. The effective symmetry is lower than spherical.

The indirect gap Si and Ge crystals have strong covalent bonding, and most chemical efforts to make particles at temperatures below 400 C have made amorphous rather than crystalline particles. Until recently this synthetic difficulty has prevented systematic studies of quantum confinement. However, we have found that crystalline, 2-8 nm diameter, faceted silicon single crystallites can be made by pyrolysis of dilute disilane at 1000 C in flowing He(4). The crystallites are briefly oxidized to give a 1.2 nm surface shell of oxide, and collected as a robust ethylene glycol colloid. TEM and Bragg powder X-ray characterization show that the Si interiors have diamond lattice

structure with lattice constant unchanged from the bulk. The average size can be varied via the initial disilane concentration, with typically a distribution standard deviation of 30 %. There is also a distribution of permanent aggregation into dimers, trimers, etc. This distribution can be physically separated into fractions using high pressure liquid chromatography. Such direct size measurement shows that crystallites of < 5 nm diameter luminescence to the blue of the bulk Si indirect gap at 1.06 micron. The smaller the size, the greater the blue shift as predicted by simple quantum confinement theory. At 2 nm diameter, the capped crystallites emit near 750 nm with about 5% quantum yield at room temperature(4). This enhanced luminescence is qualitatively consistent with the predicted intensification of oscillator strength due to quantum confinement. The quantitative, quantum mechanical nature of the emitting state is presently under investigation.

**ACKNOWLEDGEMENT:** This work has benefitted from the stimulating and supportive research environment of AT&T Bell Laboratories. I greatly appreciate collaboration with numerous colleagues, some of whom are mentioned in the references.

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# Chemical Synthesis of Nanoscale Silicons and Their Optical Properties

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A new approach to forming nanoscale silicon structures, chemical synthesis, is summarized. Figure 1 shows the dimensional hierarchy of silicon backbone materials.<sup>1</sup> The upper route shows the systematic variation from disilane (0-dim.) to crystalline silicon (3-dim.) through polysilane (1-dim.) and planar polymer (2-dim.). Oligomers have network dimensions between zero and one. Ladder polymers and superlattices also have intermediate dimensions. The lower route corresponds to the cluster structures with network dimensions between zero and three. The center route shows disordered materials, which could be formed by the plasma decomposition of silane or disilane gas.<sup>2</sup> The effective network dimensions depend on the hydrogen content, which can be controlled through the plasma power, gas pressure, substrate temperature and so on.

One-dimensional and two-dimensional silicon networks correspond to the backbone structure of polysilane and polysilyne or siloxene, respectively. They can be synthesized by Wurtz-type reaction from organodichlorosilane and organotrichlorosilane using molten sodium as a catalyst.<sup>3</sup> They are typical examples of ultimate quantum wire and quantum plane, respectively. An ultimate quantum dot structure, octasilacubane, can be obtained from tert-butyltrichlorosilane.<sup>4</sup> Furthermore, a one-dimensional superlattice structure can be formed on the main chain of a Si/Ge ordered copolymer, which is obtained from the polymerization of dichlorosilane having a unit cell backbone.<sup>5</sup> These chemical processes are summarized in Figure 2.

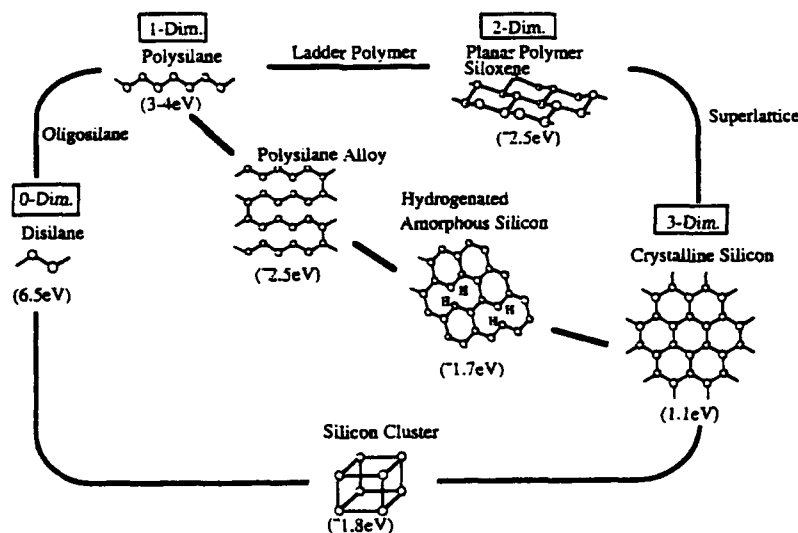


Fig.1 Dimensional Hierarchy of Si-Based Materials



Theoretically, polysilane with trans-conformation has a direct-allowed type band structure.<sup>6</sup> A two-dimensional network polymer, polysilyne, has a band structure intermediate between indirect and direct.<sup>7</sup> One-dimensional superlattices have zone-folded band structures.<sup>8</sup> The electronic structure of silicon clusters strongly depends on the cluster structure.<sup>9</sup> Figure 3 shows the photoluminescence spectra for silicon backbone materials. One of the most striking features is that almost all silicon backbone materials except for crystalline silicon can emit light. The wide wavelength region between ultra-violet and infrared can be covered just by using various forms of silicon networks.

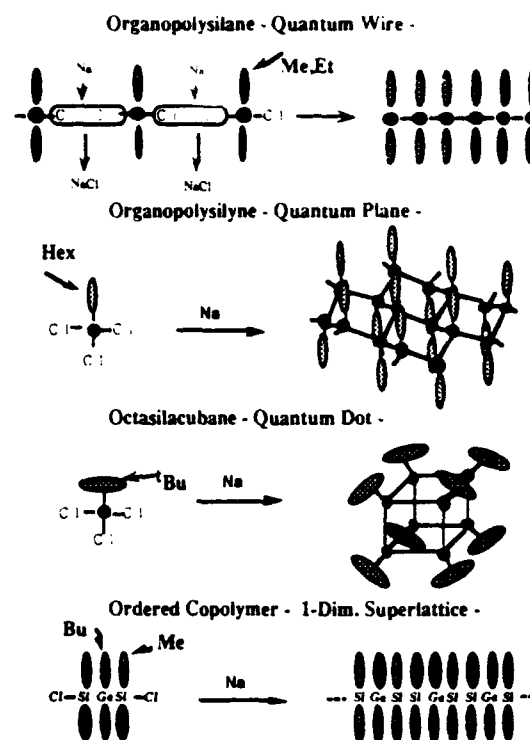


Fig.2 Chemical Synthesis Methods

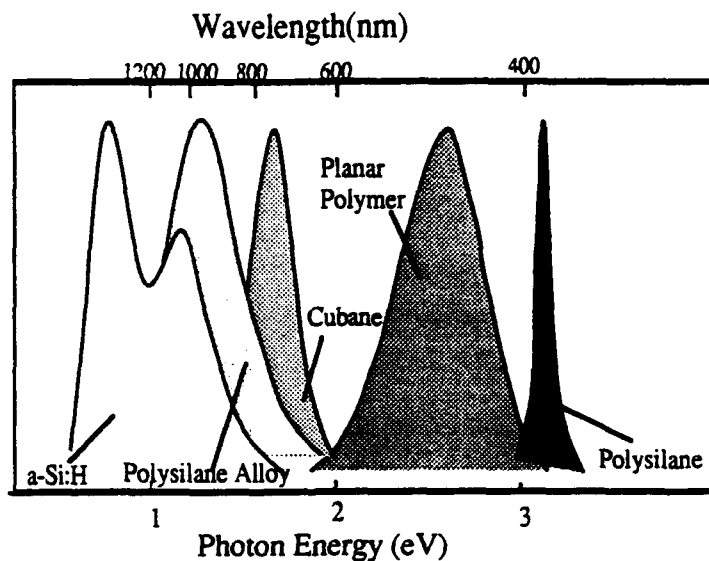


Fig.3 Photoluminescence Spectra of Si-Based Materials

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## Radiative Isoelectronic Impurities in Silicon and SiGe Alloys

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Since the discovery, in the early 1960's, of the selection rules which fundamentally limit the efficiency of optical transitions in indirect-gap materials, scientists have studied various impurity-mediated mechanisms for efficient light emission. The first materials system which received a good deal of attention was the GaAsP system, which exhibits an indirect gap for high phosphorus concentrations. It was this system which gave birth to both theoretical and experimental studies of isoelectronic impurity complexes in semiconductors. Since that time, for both practical and fundamental reasons, attention has been given to the formation and properties of isoelectronic complexes in silicon. These investigations have included damage-related centers as well as complexes containing Li, Be, C, Fe, Cu, and the entire family of chalcogen impurities.

Perhaps the most important property of an isoelectronic complex is the ability to bind an exciton and provide an efficient path for radiative recombination between electrons and holes. After presenting a short historical perspective on radiative recombination in indirect-gap materials, we will describe the general concept of an isoelectronic impurity complex. On a practical level, isoelectronic impurity complexes can differ greatly in their formation kinetics and temperature stability. Two examples which will be presented in some experimental detail include the Be-Be pair and the family of Chalcogen-related complexes. Other centers, particularly those which have been successfully excited in electroluminescence, will also be described. We will also discuss the challenges of achieving the carrier and optical confinement necessary for efficient electroluminescent devices and lasers within the constraints of a silicon materials system.

Finally, we will discuss the more general issues of binding energy and temperature stability. We examine, in particular, the formation of Be complexes in SiGe alloys and quantum well structures, and show how a comparatively simple model of the impurity potential can predict energy shifts to good accuracy.

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## **VII. FABRICATION OF NANO STRUCTURE**

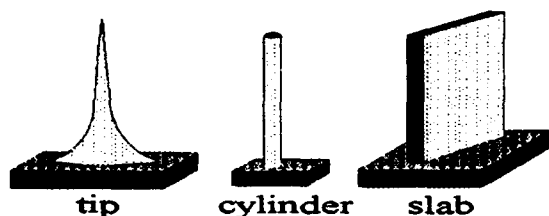
## SILICON TOOTHPICKS\* (\*and other small shapes)

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**Introduction:** The evidence presented in this Workshop argues that porous silicon fluoresces even without the presence of siloxane. Attempts to model this behavior, though, seem frustrated by the lack of a clear understanding of the morphology of the basic unit of quantum-size silicon and how these units are put together. Some excellent TEM images suggest that the quantum units are some 2-5 nm in size, perhaps connected with each other and perhaps not. One problem with TEM analysis is that the electron irradiation during analysis generates displacement damage in the silicon which can quickly degrade an image, and the presence of small "connective tissue" of silicon between the basic units could easily escape detection.

It seems clear that another type of silicon sample is needed for experiments on photoluminescence and electroluminescence---one in which the silicon morphology is well defined. Such structures might be prepared by borrowing from the technology and lessons learned in other fields. Small silicon structures in the  $\mu\text{m}$ -range and below are made with lithographic methods combined with various types of silicon etching techniques for a variety of new device applications in the fields of microelectromechanical systems (MEMS) and vacuum microelectronics. This combination of lithography and etching (dry etching, wet etching, oxidation, anodization) allows the experimenter freedom to create a variety of small shapes. Once formed, these small shapes can be further reduced to quantum dimensions by controlled oxidation. Controlled thermal oxidation is particularly attractive as a final sizing tool because of a decrease in the oxidation rate with increasing radius of curvature which slows down the reaction just in the region where control is most needed. This paper presents some thoughts on how to prepare such quantum-size silicon structures.



**Some considerations in making small structures:** Small silicon structures can be prepared with quantum sizes (2 nm) in all three dimensions (tips), two dimensions (cylinders) or in one dimension (slabs). In order to assess the geometric advantages of any one structure with

respect to the others (and assuming these lithographically-defined structures can be made to luminesce) and to porous silicon, it would be useful to define a figure-of-merit by calculating the total light emission area per  $\text{cm}^2$  substrate surface, and use this parameter as a basis for comparison. Such a calculation depends on certain assumption made regarding processing:

Assume that e-beam lithography is used for all three shapes and that the features can be placed on 0.1  $\mu\text{m}$  centers (0.1  $\mu\text{m}$  repeat unit). Tips, which require both wet and dry etching, can probably be made with the light-producing region confined to a vertical distance of  $\sim 20$  nm. Aspect ratios (height/thickness) for the oxidized cylinders and slabs are unlikely to be much larger than 100:1, so that the vertical extent of these latter two structures is assumed to be 0.5  $\mu\text{m}$ . As a comparison, porous silicon is assumed to consist<sup>1</sup> of  $10^{18}$  quantum-

size structures per  $\text{cm}^3$ , each 4 nm in diameter; we assume a vertical extent also of 0.5  $\mu\text{m}$ :

emission area per  $\text{cm}^2$  substrate

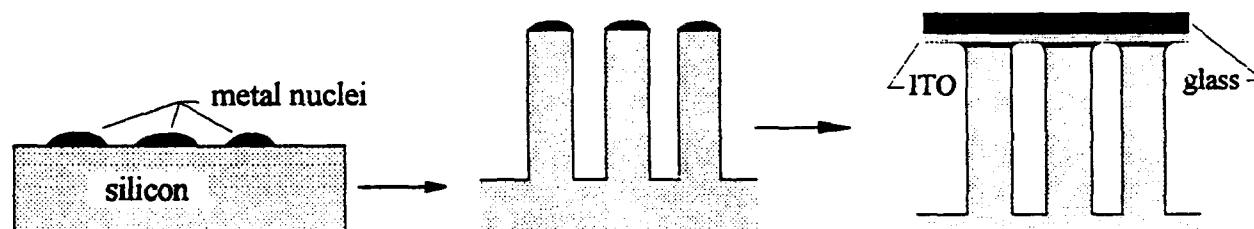
tips	cylinders	slabs	porous Si
$4 \times 10^{-10} \text{ cm}^2/\text{cm}^2$	$0.5 \text{ cm}^2/\text{cm}^2$	$10 \text{ cm}^2/\text{cm}^2$	$25 \text{ cm}^2/\text{cm}^2$

If luminescence can be made to occur in a structure with only one-dimensional quantum confinement, then a close-packed array of thin slabs might be the best configuration to use.

**Methods for making small structures:** The precursor structures (before final oxidation "sizing") are made as follows: Tip precursors are made<sup>3</sup> by a i) lithographic definition of an oxide mask, ii) dry etching  $\sim 100 \text{ nm}$ , and iii) wet etching. Cylinders and slabs are made by i) and ii) only, although slabs may be made on {110} silicon by anisotropic etching which forms slabs with {111} faces.

Precursor cylinders can also be made in an array sandwiched between two plate electrodes, suitable for electroluminescence studies, by using the method of VLS whisker growth<sup>2</sup>. The metal must form a eutectic with silicon, the vapor contains an agent for growing silicon (such as  $\text{SiCl}_4 + \text{H}_2$ ), and the temperature (which controls the thickness) is in the range 600-1000°C:

Electroluminescent package using VLS growth



**Oxidation sizing:** Oxidation rates become slow as curvature increases<sup>4</sup>, leading to the formation of edges and tips with radius of curvature  $\sim 0.5 \text{ nm}$ . This trend is independent of the effect of geometry alone (which produces an opposite trend<sup>5</sup>) and only occurs at temperatures below  $\sim 1100^\circ\text{C}$ ; this is because the reduced oxidation kinetics is due to strain energy created during oxidation,<sup>6</sup> and at higher temperatures the lowered viscosity of  $\text{SiO}_2$  permits the oxide to flow, relieving the strain. Rates are lowered more for a hemispherical tip than for a cylinder of the same radius, so that isolated silicon islands can be created above the tips, imbedded in a sea of oxide; further oxidation oxidizes the spherical silicon leaving only the atomically-sharp tips. Because of the dependence of oxidation rate on diameter, small diameters are "self-adjusting" and a cylinder of constant diameter is maintained, enhancing the likelihood of generating 4 nm-diameters columns with a 100:1 aspect ratio. The oxidation kinetics of very thin ( $< 10 \text{ nm}$ ) slabs has not been studied, however, and it is not certain whether thin large-area slabs can also be made.

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## Field Emission Properties of Air Exposed Si FEAs

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Field emitter array (FEA) emitter tips and p-Si structures have similar size and surface chemistry. The combination of electronic properties present in porous Si (p-Si) which lead to visible luminescence may also play a role in the field emission process from Si field emitter arrays (FEAs).

FEA technology is being developed in many labs around the world for diverse applications including flat cathodoluminescent displays, fast rectifiers, and RF power amplifiers. High speed devices would benefit if the FEAs developed high transconductance at lower current<sup>1</sup>. Si is often used to fabricate FEAs because much of the required processing technology is relatively well developed. The oxide Si normally forms upon exposure to air provides a robust surface, but the tunneling probability through the oxide should be small according to simple models<sup>2</sup>. In fact, the maximum emission current obtained from many Si FEAs is often low ( $<100\text{nA}/\text{tip}$ ), despite very small tip radii. However, several groups have reported emission of  $10\mu\text{A}$  per emitter tip (roughly  $10^7\text{A}/\text{cm}^2$  locally) from air-exposed Si FEAs<sup>3</sup>. This large current density suggests that some mechanism is increasing the tunneling probability. One possibility is that the oxide is reduced or removed by the emission process. Alternatively, emission might occur directly from surface states. The p-Si results suggest that this latter process may be more important than previously suspected.

The discrete spectral luminescence bands measured from p-Si and the correlation of the relative intensities from the bands with surface hydrogen and oxygen suggests: 1) Surface states provide the dominant path for visible wavelength recombination. 2) Electron-hole pair relaxation to bulk Si energies is reduced enough to allow population of the surface states. An increase in the band gap of the p-Si particles due to either quantum confinement or stress could alter the bulk band structure enough to reduce thermalization to lower energies. Because the Si FEA emitter tips are similar to the p-Si particles in size and surface chemistry, there is reason to believe that the two have similar electronic structures. Both an increased

band gap and the presence of surface states could improve the tunneling probability from air-exposed Si field emitters.

If confinement effects are responsible for visible p-Si luminescence, confinement effects could easily affect the Si FEAs as well. Although good measurements are typically difficult to obtain, the FEA tip radii are probably often less than 100 Å. Solution of the Poisson equation assuming bulk Si band structure and external fields typical for field emission from larger tips ( $5 \times 10^7$  V/cm) shows that accumulation at the surface would force electrons into states over 0.3 eV above the Si band gap minimum in a surface layer a few Å wide. This accumulation reduces the tunneling barrier and increases the density of electrons, thus vastly increasing the field emission current. If quantum confinement were significant, the tunneling barrier would be reduced still more. Although the density of states at the Fermi level would be also be reduced, the net effect would still be an increase in field emission current. Stress might change the surface dipole (electron affinity) as well increase the band gap, hence the effect on field emission is more difficult to predict.

Assuming that the Si FEA emitters are covered with oxide, field emission directly from a high density of occupied surface states, rather than through the oxide, is required to achieve the performance needed for many high frequency device applications. The luminescence data from p-Si, as well as the high emission currents measured from Si FEAs strongly suggests that high concentrations of these states do exist under some conditions. The broad luminescence bands obtained from p-Si suggests that the states have high density. The high field just inside the surface of a Si emitter implies that significant numbers of "hot" electrons will approach the surface with energies well above the Fermi level. Together with accumulation, possibly increased by confinement, this effect increases the probability that surface states well above the conduction band minimum can be repopulated, thus sustaining field emission.

Further developments in either p-Si or FEA research may have implications for the other area.

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## Extending the Photoluminescence of Crystalline Si to other Structures and Compounds

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45221-0030

The on-going research effort at the University of Cincinnati on light emission from Si has concentrated on the following major directions : (1) understanding the origin and mechanisms for photoluminescence (PL) in porous Si (PoSi); (2) investigation of PL from alternate Si-related materials and structures; (3) development of device structures incorporating PoSi and/or other related compounds for various optoelectronic applications.

We have investigated the PL of stain-etched PoSi on films with varying degrees of crystallinity. Si films deposited at low temperatures ( $<600^{\circ}\text{C}$ ) yielded an amorphous structure and were not luminescent upon etching. On the other hand, Si films deposited at  $600^{\circ}\text{C}$  and above exhibited a polycrystalline structure and resulted in copious photoluminescence after stain-etching. *It, therefore, appears that a minimum level of crystallinity is required for photoemission in PoSi.* The relationship between crystallinity, surface morphology, and optical properties of PoSi will be discussed.

Light emission from PoSi has triggered considerable interest in exploring related Si materials that may have similar properties. We have investigated several Si compounds and structures, including siloxene, silicon carbide/silicon heterostructures and silicates. We have observed PL from all of these materials or structures, in some instances without the need for chemical treatment. We will compare the PL results from these Si compounds and discuss differences and similarities to each other and to PoSi.

A key element for any optoelectronic application is the ability to produce light in selected regions. We have found that the incubation time ( $t_i$ ) for the onset of PoSi formation by stain-etching in  $\text{HF:HNO}_3\text{:H}_2\text{O}$  is a strong function of dopant type and concentration. We have utilized the difference in  $t_i$  between n- and p-type Si to produce *selective area photoluminescence* (PL) by  $\text{Ga}^+$  focused ion beam (FIB) implantation doping and  $\text{B}^+$  broad beam implantation doping of n-type Si. Using 30 kV FIB  $\text{Ga}^+$  implantation, PL patterns with sub-micrometer resolution have been obtained for the first time.

A potential application of PoSi is in the area of flat-panel displays. For this purpose we have utilized poly-Si thin films deposited on quartz substrates. Under UV excitation, the stain-etched doped and undoped poly-Si films produce uniform orange-red ( $\sim 650\text{ nm}$ ) luminescence very similar to that obtained from stain-etched crystalline Si substrates. Luminescent patterns with sub-micron ( $\sim 0.5\text{ }\mu\text{m}$ ) dimensions have been obtained in PoSi produced from poly-Si films.

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# VACUUM MICROELECTRONICS

INTERNATIONAL WORKSHOP ON LIGHT EMISSION AND ELECTRONIC PROPERTIES OF NANOSCALE SILICON  
CHARLOTTE, FEB. 1-3, 1993

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## Introduction:

Vacuum Microelectronics is a potentially emerging technology based on the use of silicon fabrication methods to build micron or submicron-scale vacuum devices, circuits, etc using field emitters, but which involves three dimensional tunnelling structures with nanometric dimensions. The progress and problems of vacuum microelectronics may therefore be of some interest to people studying light emission from nanometric silicon. What makes vacuum microelectronics possible is the replacement of thermionic electron sources, which have low and unreliable current densities, with field emitters, which run fairly cold, and which provide current densities of up to  $10^8$  A/cm<sup>2</sup> [1] from sharp points of nanometric radius at electric fields of  $10^7$ - $10^8$  volts by quantum tunnelling. These tips ordinarily must have strong interatomic bonds, because at not much higher values the tips are unstable against morphological changes and atomic or ionic emission.

What makes this possibly practical is the use of silicon-like fabrication techniques to produce integral insulated extraction electrodes well-aligned to the emitters, so that low voltages result in high fields at emitters. These ideas occurred early to workers at SRI who devised the field emitter array structure sketched in Fig.1 [2]. The ingenious fabrication scheme illustrates the problem of fabricating arrays of integrated field enhancement structures with 3-D nanometer design rules, i.e. well beyond the limits of conventional lithography. Starting with a silicon or glass substrate with a 1 micron insulator and a half-micron Mo metallization, intended as the eventual extraction electrode, they e-beam pattern 1 micron resist openings on 2-3 micron centers, and RIE down to the Si or glass substrate. Through these openings Mo is e-beam deposited vertically at the same time the holes are being closed up by depositing a "parting layer" at grazing incidence. That forces the Mo deposition into a cone with 15 nm tip radius. The parting layer can then be etched off. Each emitter can produce tens of microamperes. This procedure self-aligns the emitter in the center of the extraction electrode hole, which is important for beam quality and for the avoidance of reregistration. XY addressing can be carried out by dividing the extraction grid into strips and in using polysilicon thin film driving electronics under the emitters, and by other methods. This scheme has been aimed at high definition flat panel displays and has been stimulated similar efforts in many countries; it can produce an extremely high density of bright and fast gray-scale pixels with 100V extraction voltage and 1000 volts on the phosphor screen.

The approach taken at NRL[3] was based more closely on ordinary silicon fabrication technology, and was aimed at multi-gigaHerz amplification at power levels beyond single device semiconductors possibilities. The approach was to use crystallographic etching to leave silicon <111> pyramids sticking out of out of a silicon <100> wafer, using oxide or nitride masking dots. This was also to be a self-aligned process with a deposited insulated extraction grid, sketched in Fig 2., in which the grid structure is fabricated using the same masking dot. It was hoped that this technology could be batch-processed with much lower unit cost, volume, and voltage than vacuum power tubes. A first planar vacuum "transistor" was demonstrated with gain in 1987, [3] and concepts for using microstrip-excited field emitter arrays to directly excite output wave guides have been analyzed. Later it was realized that <111> etched pits, or antipyramids, were much more controllable than free standing pyramids, because of the bonding at the intersections of the <111> faces, and that these could be used as mold for deposited metal tips [4].

Lower voltage vacuum microelectronic devices can be produced using emitters with smaller tip radii; techniques of tip formation by various techniques are known which can produce tips of 1 nm in silicon or metals by oxidation[5] or by acid etching. In such structures quantum confinement is strong but 2-dimensional, somewhat like porous silicon. However, it does not seem likely that such tips can be produced reproducibly in arrays, and it is not clear whether they can be stable enough for reliable operation. At least in the short run, reproducibility and reliability seem to militate against tip radii of less than 10 nm. Silicon structures are attractive because pn junctions for emission limitation, or transistors destructive runaway. It is also true that velocity saturation provides a natural current limiting feature in silicon emitters. On the other hand in semiconductor emitter tips, there can be strong

field penetration in semiconductor emitters, so that surface fields are weaker than in metal tips of the same shape.

We have incomplete knowledge and control of tunnelling mechanisms and of noise mechanisms. Recently, at Charlotte, an exact elastic tunnelling method[6] for linear barrier potential models has been developed, based on a integral representation in the complex plane of the solution of the 1-D Schrodinger boundary value problem. This exactly satisfies the outgoing-wave boundary condition at infinity. That provides a start for a perturbation calculation for potentials which include the image force and avoids the use of unsatisfactory WKB methods. It appears that the unphysical and divergent classical image theory will not work, and a realistic model for metals or dielectrics is needed which may be interesting for nanometer crystallite tunnelling. Tsu has pointed out[7] that quantum confinement effects in the Penn dielectric gap modulate the image potential.

Adatoms have an observable effect on tunnelling current noise, a problem which vacuum microelectronics must overcome. Furthermore Ohmic and Nottingham heating[1] will cause temperature changes influencing both Taylor force morphology changes and adatom desorption and surface diffusion kinetics. This may be the origin of flicker noise in emission[8]. There is no significant "space charge cushion" to smooth out current noise.

The conclusion is that vacuum microelectronics shares some of the problems of quantum confined porous silicon, including nanoscale fabrication, tunnelling, etc. but does not appear to shed much light on the light emission mechanism itself from porous silicon.

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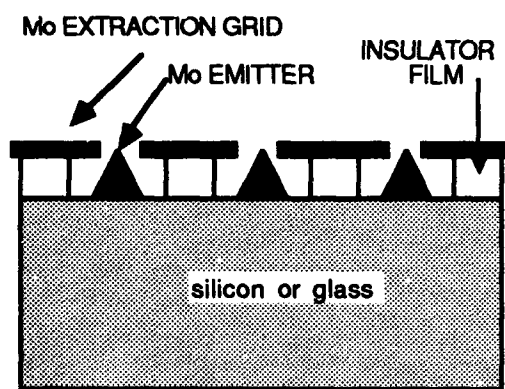


Fig. 1 SRI FIELD EMITTER

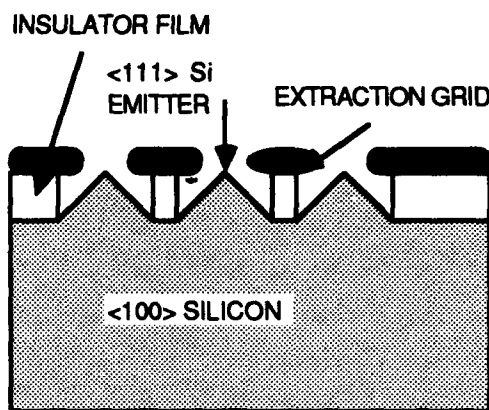


FIG. 2 NRL FIELD EMITTER

## SILICON NANOFABRICATION WITH THE STM

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The scanning tunneling microscope (STM) offers an alternative to short wavelength photon, ion or electron beam lithography for the production of nanodevices. The strength of the STM approach lies in its inherently high spatial resolution and low-energy beam; its greatest current weaknesses are a lack of detailed understanding and a serial approach. However, this is a very new technology and rapid progress is being made; there is every reason to expect this methodology to acquire an increasing role as the size of devices decrease toward molecular dimensions. As an STM probe approaches a surface, it first produces an electron beam, then a strong electric field and finally chemical forces are added. Each of these offers an opportunity to produce nanostructures or even single-atom changes in a sample. The construction method can be based on exposure of a resist, inducing surface reactivity that leads to CVD or etching, moving atoms of the sample, and transferring atoms between sample and probe at designated locations. All of these effects have been demonstrated, but comprehensive understanding is not yet available and the art is still highly experimental.

The strong worldwide interest in silicon luminescence clearly results from the many unique and fortuitous properties of silicon, which are responsible for its role as the leading VLSI and micromachining material. This unique character of Si is borne out in by the current status of STM-based nanofabrication; the most exceptional structure manipulations yet reported have been achieved with Si. Lyo and Avouris [1] have removed single Si atoms from a Si surface and deposited them at other, chosen locations. Moving their probe slightly closer to the surface, they achieved the same type manipulations with 10-50 atoms at a time. These manipulations are attributed to a combination of field and chemical forces. In our laboratory [2], we have constructed narrow silicon columns on initially flat silicon crystal surfaces, by dragging atoms across the surface and up toward the probe tip. Again, this is believed to result from a combination of field and chemical forces. These columns have height/width > 1 and can be made with diameters of 1-10 nm as desired for Si luminescence. Based on metal manipulations in our laboratory (unpublished), and metallic transfers reported in the literature [e.g. 3], interconnects to these columns can also be produced with STM manipulations. Thus, STM based production of silicon luminescent devices appears quite feasible.

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## **Nanofabrication of Group IVA Semiconductors: The Chemistry of Size and Shape**

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Liquid-solution phase syntheses are being developed as a route toward fabricating Si and Ge single crystals with sizes near and below the dimensions relevant for quantum confinement. Although this research is still at an early stage, it is becoming apparent that such synthetic pathways may be useful not only for the control of crystallite size, but also for the control of crystallite shape. The synthesis of single crystal Si and Ge quantum dots, as well as the synthesis of single crystal Ge quantum wires will be discussed.

# Photoluminescence from Nanocrystalline Ge Formed By A New Method: High Pressure Oxidation of $\text{Si}_{0.6}\text{Ge}_{0.4}$ Followed by $\text{H}_2$ Reduction of $\text{Si}_{0.6}\text{Ge}_{0.4}\text{O}_2$

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At Brown University we have developed a new method for the synthesis of nanocrystalline Ge embedded in  $\text{SiO}_2$  that, like similar materials produced by co-sputtering of  $\text{SiO}_2$  and Ge (e.g. (1)), show strong visible photoluminescence. Samples were synthesized from high purity  $\text{Si}_{0.6}\text{Ge}_{0.4}$  epitaxially grown on  $\langle 001 \rangle$  Si substrates. The nanocrystal formation is done in a two step process of high pressure oxidation at low temperature ( $\approx 500^\circ\text{C}$ ) followed by annealing at  $750^\circ\text{C}$  in flowing forming gas ( $80/20:\text{N}_2/\text{H}_2$ ). The high pressure oxidizing conditions are created using either steam at 25 MPa and  $475^\circ\text{C}$  (2) or dry high pressure  $\text{O}_2$  at 70 MPa and  $550^\circ\text{C}$  (3). High pressure oxidation conditions ensure that a compositionally congruent oxide of  $\text{Si}_{0.6}\text{Ge}_{0.4}\text{O}_2$  is formed from the original alloy. After oxidation, the  $\text{GeO}_2$  in the oxide is reduced by  $\text{H}_2$  during annealing at  $750^\circ\text{C}$ . The gas chemistry is selected so that the  $\text{SiO}_2$  network is unaffected while the  $\text{GeO}_2$  is reduced to elemental Ge which is distributed through the oxide as nanocrystalline precipitates. The samples were analyzed using Raman spectroscopy, cross sectional TEM, and the 488 nm line of an  $\text{Ar}^+$  laser for photoluminescence excitation. As-oxidized (i.e. unprecipitated) samples show no photoluminescence peak, while a broad photoluminescence band, peaked at 2.14 eV (580 nm) with a full-width-at-half-maximum of 0.3 eV, was observed in samples that were annealed at  $750^\circ\text{C}$  in flowing forming gas for 10, 30 and 60 minutes (4). With  $10 \text{ W/cm}^2$  illumination, samples annealed for 10 minutes at  $750^\circ\text{C}$  show PL that is clearly visible to the unaided eye. The average particle size increases and the intensity of the photoluminescence decreases with increasing time at temperature.

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# Nanochannel Glass Arrays as a Potential Lithographic Mask for Patterning Silicon

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Nanochannel glass materials<sup>1</sup> are glass composites with parallel uniformly shaped voids or channels arranged in periodic arrays. The glass material has been fabricated with channel diameters on the order of 10's of nanometers and packing densities as high as  $3 \times 10^{10}$  channels per square centimeter. The channel glass typically contains greater than  $10^6$  channels in an array. The high temperature stability of the nanochannel glass is well suited as a host or template for the formation of high definition semiconductor structures or as a mask for massively parallel patterned lithographic applications.

Initial attempts at pattern transfers from the nanochannel glass matrix to silicon substrates has been accomplished at temperatures between 550 – 600°C. Controlled oven atmospheres are essential in the pattern transfer process. SEM micrographs indicate a clear demarcation between regions on the silicon substrate in contact with the glass at elevated temperatures from those not in contact. Substrate contact regions heated above 550°C in air contain a thin layer of glassy material while those below 550°C maintain the original smooth polished surface of the substrate. In both cases, a thin layer of oxidized potassium exists in the channel area not in contact with the glass at elevated temperatures. The potassium oxide is not present when the system is heated under vacuum. By utilizing the anisotropic etching properties of [110] silicon surfaces, it may be possible to etch a replica of the inverse of the nanochannel glass pattern into the silicon substrate.

Further work is currently under way to transfer smaller patterns to silicon and other substrates, and to characterize these small structures as their size approaches the quantum regime.

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Structure and Photoluminescence Properties of Porous Silicon  
Prepared by Spark Erosion

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Abstract

Photoluminescence studies have been performed on porous p-type as well as n-type silicon wafers which have been treated in air or in a dry nitrogen atmosphere, utilizing a high frequency, high voltage, spark erosion technique. This sample preparation, which does not involve aqueous solutions or any contaminants, yields photoluminescence spectra similar to those obtained by anodic etching in HF or unbiased etching in various HF-containing reagents (Figure 1). Visible, red light has been observed when illuminating spark eroded silicon with UV radiation ("black light"). Fourier transform infrared spectra reveal that the dominant features in spark eroded silicon are the Si-O-Si stretching mode and the Si-O-Si bending mode. No infrared vibrational modes characteristic for hydrogen involvement or siloxene have been found in spark eroded Si. Results from x-ray and electron diffraction studies suggest that spark eroded Si involves polycrystalline silicon.

High resolution transmission electron micrographs of spark eroded silicon reveal (among other features) silicon crystallites in the 4-8 nm range which are imbedded in an amorphous matrix (Figure 2) which has been identified by EDS to be SiO<sub>2</sub>. The depth of the porous layer was found to increase linearly with increasing spark erosion time (Figure 3).

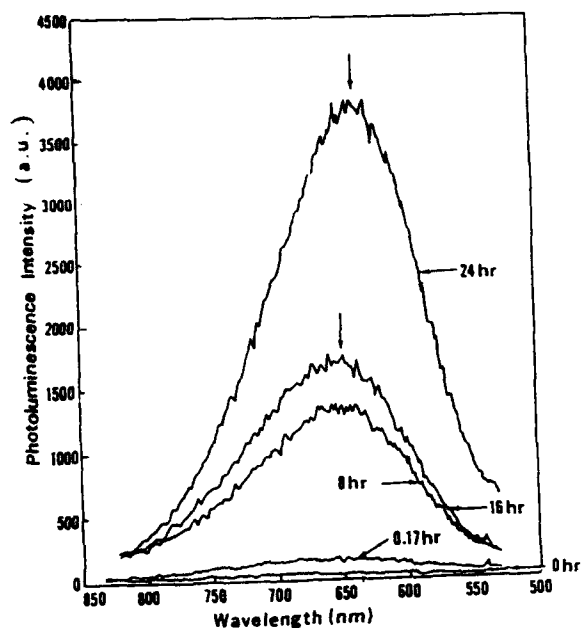
During the Charlotte, NC, workshop, it has been suggested that spark erosion yields similar photoluminescence spectra as known for irradiated, that is, damaged, silica. Indeed, high energetic x-rays, neutron irradiation, and electron irradiation of fused silica (SiO<sub>2</sub>) have been observed by others to yield photoluminescence bands having peak energies at 2 eV, 4.8 eV, 5.0 eV, and higher energies. The PL bands have been ascribed in the literature to non-bridging oxygen hole centers. To decide on this point, we conducted experiments in which we dipped spark eroded Si for various times into HF in order to dissolve the (native) SiO<sub>2</sub>. No decrease in PL intensity was observed. The peak shifted slightly into the blue region. This suggests that defects in SiO<sub>2</sub> or undamaged SiO<sub>2</sub> are not the major cause for PL in spark eroded Si.

We have also conducted PL measurements on amorphous, non-porous silicon (obtained by Si-ion implantation into a silicon substrate). We have found virtually no photoluminescence for these amorphous silicon samples.

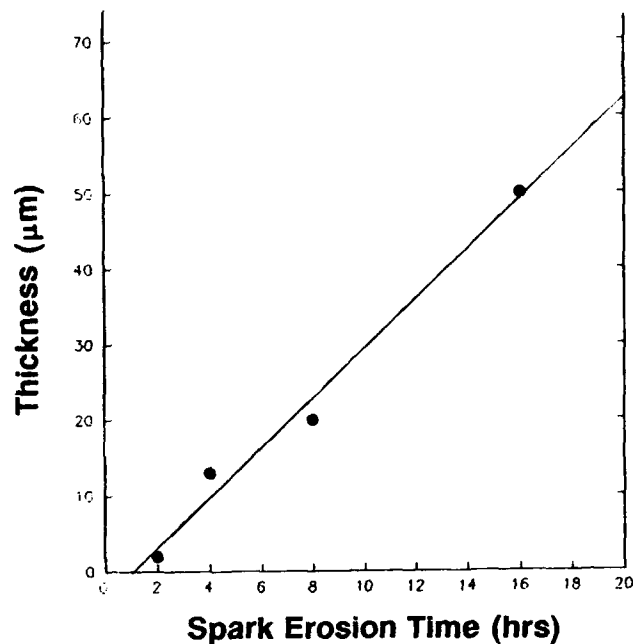
We conclude that spark erosion yields nanocrystallites imbedded into an amorphous matrix. The mechanism(s) for spark eroded photoluminescence do not involve hydrogen, damaged silica, amorphous silicon, or siloxene.

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**Figure 1.** Room temperature photoluminescence spectra of porous, p-type silicon submitted to spark erosion in air for various time intervals.



**Figure 3.** Depth of porous silicon layer submitted to various time intervals to spark erosion.



**Figure 2.** High resolution TEM of spark eroded silicon.



## Optical and Electronic Properties of Ordered Semiconductor Alloys

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Ordered semiconductor alloys form an interesting class of materials which spontaneously order during epitaxial growth. Because of this phenomenon, these materials exhibit modified optical and electronic properties. In particular, the reduced symmetry that accompanies the ordering results in a lowering of the band gap and a splitting of top of the valence band into light hole and heavy hole like states. This makes materials that ordinarily are not polarizable efficient light polarizers at photon energies above the band gap. Because ordering on the sublattices is equivalent to superlattice formation, electro-optic applications, similar those currently being utilized in the GaAs/AlGaAs system are also possible. Furthermore, it is known that in many ordered systems ion beam damage can be used to induce disordering allowing for the formation of nanostructures, such as quantum wires and dots that have only one surface that is exposed to the ambient. In this way it may be possible to avoid problems arising from Fermi-level pinning at free surfaces.

While other groups have demonstrated band gap narrowing in the ordered phase, there has been little work on the complete band structure of ordered alloys as well as no consideration of the effects of incomplete ordering as defined by the intermixing of the A and B sublattices in the case of  $ABC_2$ . At NRL, we have used polarized spectroscopy such as electroreflectance, photoreflectance and photovoltage to study the band structure of  $GaInP_2$  for energies in the range of 1.5eV to 4eV. From our work, we show that there are valence band splittings produced by the reduced symmetry that are polarized. We have related the magnitude of these splittings to the degree of ordering in the system and show how optical spectroscopy can be used to characterize the disorder in terms of intermixing of Ga and In sublattices, rather than the formation of ordered regions in a disordered matrix. Because of the tunability of the band gap of GaInP, with ordering, it is possible to have tunable electro-optic devices spanning 200 meV of the optical spectrum in the range of 1.7 to 1.9 eV. We are also studying ordered magnetic alloys, such as ZnFeSe, which have band gaps in the near UV.

## Light Emission from Si-based Superlattices

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### Abstract

There is a continued interest in the exploration of Si-based light emitting devices for optoelectronic applications. The indirect nature of Si and Ge bandgap requires band structure perturbation in order to enhance the luminescence efficiency to a practical level. The approaches used to date include the engineering of the band structure of Si using artificial superlattices, rare earth doping, SiGe alloys and the use of quantum size effects of nanostructures. At UCLA, we have investigated luminescence from short period  $\text{Si}_m\text{Ge}_n$  monolayer superlattices and SiGe/Si quantum well structures [1, 2, 3, 4]. In the case of superlattices, if the periodicity and strain configuration are properly chosen, the minimum of the indirect conduction band may be folded back to the  $\Gamma$  point producing a quasi-direct bandgap material. We have studied such superlattices with different periodicities using photoluminescence to probe the band folding effects. The superlattices are symmetrically strained by growing on relaxed buffer layers in order to provide in plane tensile strain in the Si layers. Theoretical calculations suggest that the possibility for observing quasi-direct bandgap is further enhanced in this strain configuration.

A typical structure consists of a  $2\text{ }\mu\text{m}$  thick  $\text{Si}_{1-x}\text{Ge}_x$  relaxed buffer layer on which the superlattice is grown. The superlattice is made of 80 periods of  $m$  Si monolayers and  $n$  Ge monolayers ( $m \times n$ ) and is symmetrically strained with the average Ge concentration in the superlattice matched to that in the buffer layer. Transmission electron micrographs (TEM) show layered structure with a low dislocation density. However, due to its strain relaxation, the buffer layer contains a high density of misfit dislocations located near the Si/ $\text{Si}_{1-x}\text{Ge}_x$  interface. Figure 1(a) shows PL spectra of an as grown  $16 \times 4$  superlattice and after etching away of the superlattice region. For the as grown sample, the transverse optical (TO) phonon assisted Si boron bound exciton luminescence at 1.093 eV, a sharp peak at 1.023 eV and a broad spectrum or background luminescence at lower energies are observed. The broad band is attributed to dislocations and perhaps other defects in the buffer layer whereas the sharp peak at 1.023 eV originates from the superlattice. This was further confirmed by progressively etching the superlattice as shown in Fig. 1(a). Similarly, a  $12 \times 4$  superlattice shows a peak at a slightly lower energy position (0.995 eV). This may be due to the different strain configuration which affects the band edge. The direct-indirect nature of the luminescence has not been confirmed to date; however, the strength of the luminescence suggests that the transition may be indirect.

We have also studied the effect of atomic hydrogen (deuterium) passivation on the photoluminescence. It was found that upon passivation, that the background luminescence nearly disappeared while a new line at 0.962 eV, a 61 meV lower in energy than the narrow line, emerges as shown in Fig. 1(b). This line corresponds to the phonon replica of the peak

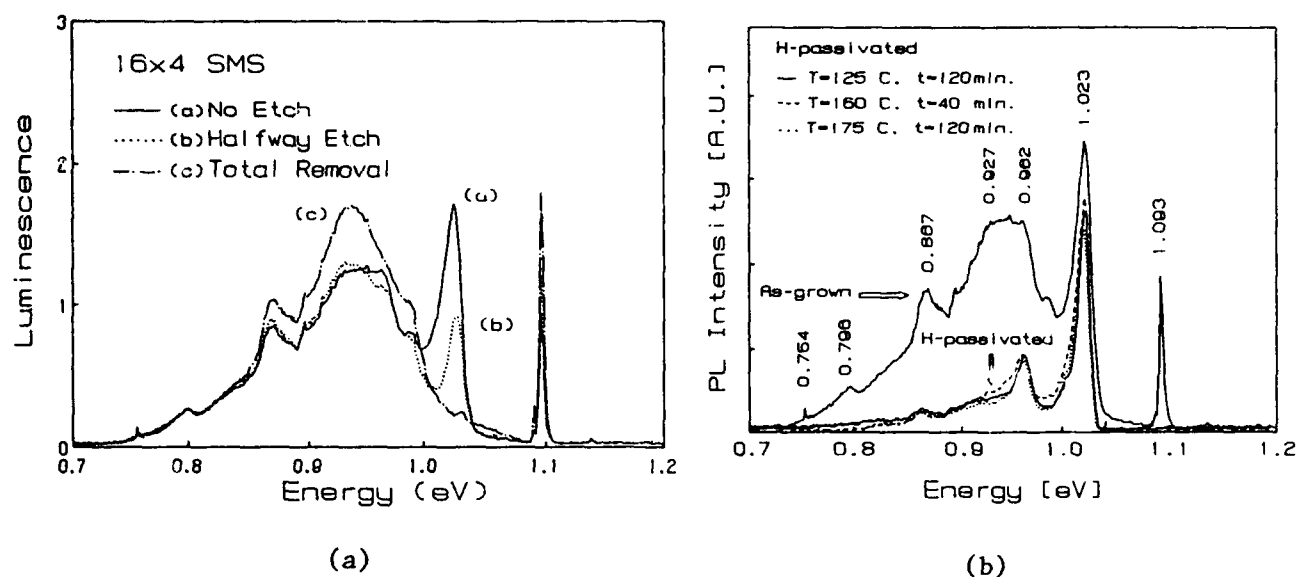


Figure 1: Photoluminescence spectra of a  $\text{Si}_{16}\text{Ge}_4$  superlattice grown on a  $\text{Si}_{0.8}\text{Ge}_{0.2}$  relaxed buffer layer (a) as-grown and gradual etching of the superlattice (b) as-grown and hydrogen passivated for three different temperatures and times are represented: 125 C for 20 min, 160 C for 40 min, and 175 C for 120 min.

at 1.023 eV. Similar behavior has also observed for the superlattice with periodicity  $12 \times 4$ . This result demonstrate that the hydrogenation is a powerful technique of discriminating defect- and bandgap-related luminescence.

More recently, we have probed the luminescence due to strain SiGe alloy layers and SiGe/Si quantum well structures. For low Ge compositions (less than 25%) intense excitonic luminescence with well resolved phonon structures have been observed. The continued progress in the material growth and band structure engineering may lead to application of these structures for Si-based light sources in the future.

Acknowledgement: The work was in part supported by ARO.

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## Visible Light Emission from Silicon and Silicon Oxide (SiO<sub>x</sub>) Nanoparticles

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Nanosize particles of silicon and silicon with oxygen were synthesized from the gas phase precursors silane and oxygen using a 100 Watt nonthermal argon microwave plasma. Oxygen dopant reactant gas flow rates were varied from zero to twice the molar flow rate of silane. Mean particle sizes were varied from approximately 7–20 nm by changing the reactor pressures from 1–8 Torr respectively. Particles were collected from the reaction chamber walls in the vicinity of the microwave plasma, or downstream from the plasma on electrostatic precipitator plates. The particles were characterized to determine their mean diameter, size distribution, crystallinity and crystalline phase using Transmission Electron Microscopy (TEM), Selected Area Diffraction (SAD), and X-Ray Diffraction (XRD). Orange-red light emission has been previously observed in silicon nanosize particles<sup>1-4</sup>. The present study has shown that particles grown with up to twice the molar flow rate of oxygen to silicon, characterized as highly amorphous, exhibit no noticeable decrease in the optical PL. This also been shown to be the case for particles grown to diameters up to 20nm. These results have implications for the mechanism of PL in silicon nanoparticles.

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## **A BRIEF SURVEY OF OTHER NANOSCALE FABRICATION TECHNIQUES**

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### **ABSTRACT:**

A number of researchers with novel fabrication techniques for nanoscale semiconductor structures, who were unable to attend this workshop, have graciously allowed us to present a brief summary of their techniques:

#### **Electroluminescence from Silicon Dioxide Films containing Tiny Silicon Islands**

**D.J. DiMaria, IBM, T.J. Watson Research Center, Yorktown Heights, NY, 10598**

**D.J. DiMaria, J.R. Kirtley, E.J. Pakulis, D.W. Dong, T.S. Kuan, F.L. Pesavento, T.N. Theis, J.A. Cutro, and S.D. Brorson, J. Appl. Phys. 56, 401 (1984).**

#### **Quantum Wire Silicon LED's**

**D.K. Biegelsen, Xerox PARC, Palo Alto, CA 94304**

**H.I. Liu, N.I. Maluf, R.F.W. Pease, D.K. Biegelsen, N.M. Johnson, and F.A. Ponce, J. Vac. Sci. Technol. B 10, 2846 (1992).**

#### **Latex Ball Etch Mask for Submicron Array**

**P.J. Stiles, Brown Univ., Providence, RI 02912**

**H. Fang, R. Zeller, and P.J. Stiles, Appl. Phys. Lett. 55, 1433 (1989).**

#### **Optoelectronic Devices from Erbium in Bulk Silicon**

**L.C. Kimerling, MIT, Cambridge, MA**

#### **Laser Ablation of Si Nanoparticles**

**S.C. Tidrow, US Army Research Laboratory, Ft. Monmouth, NJ 07703**

#### **Pulse Power Fabrication Technique for Silicon Nanoparticles**

**T. Burke, L. Kingsley, M. Weiner, and C.G. Thornton**

**US Army Research Laboratory, Ft. Monmouth, NJ 07703**

#### **CVD Deposition of Si Micro-columns**

**W.R. Sinclair, W. Robert Sinclair Associates, Summit, NJ 07901**

**R.A. Lux, US Army Research Laboratory, Ft. Monmouth, NJ 07703**

VIII.

SILOXENE

# SILOXENE: LUMINESCENCE FROM TWO-DIMENSIONAL SILICON STRUCTURES

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Luminescence in silicon-based materials can be achieved through various methods of localising charged carriers: structural disorder in amorphous silicon, confinement to one-dimensional chains in polysilanes or, as proposed as the origin of the luminescence from porous silicon, confinement to small crystallites. Another method is the confinement to two-dimensional silicon planes which is realised in a class of materials called siloxene. In the context of the recent investigations of porous silicon, we have conducted an extensive study of the properties of siloxene which is summarized. Emphasis is given to the photoluminescence and its excitation spectroscopy and to the microscopic identification of the radiative transitions with the help of optically detected magnetic resonance. The results obtained on siloxene are compared to those from porous silicon.

Siloxene has been long known for its photoluminescence properties unusual for a silicon-based system. The material is synthesised from  $\text{CaSi}_2$ , consisting of alternating layers of Ca and Si, the latter being essentially the 111-double layers found in crystalline silicon. The intercalated calcium atoms can be extracted with aqueous HCl, which leaves the silicon layers passivated with H- and OH-groups, resulting in the overall stoichiometry of  $\text{Si}_6\text{O}_3\text{H}_6$ . X-ray diffraction and STM studies show that the material obtained is again a layered structure, the lattice constant in the layers is only about 0.5% smaller than that of crystalline silicon, while the spacing of the layers is approximately 6 Å. The substance exhibits a strong photoluminescence, which can be in the blue or in the green/yellow region of the spectrum depending on the exact preparation conditions.

It turns out that the structure just described is metastable. Under the influence of temperature or UV-light, the oxygen atoms of the ligands will flip into the silicon layer forming Si-O-Si bonds, the hydrogen taking the role of the sole bond terminator. The energy gain per oxygen atom can be calculated to be about 1 eV. The resulting highest symmetry structure is that of rings formed of six silicon atoms ( $\text{Si}_6$ -rings) which are linked to each other by these oxygen bridges. This structural modification is accompanied by a drastic change in the electronic properties of the material. Theoretical calculations show that the band structure is changed from containing a direct bandgap as the lowest optical transition to an indirect bandgap. Due to the spatial confinement of the charged carriers in the ideal  $\text{Si}_6$ -rings the transition probability stays high, enabling the high quantum efficiency of the luminescence.

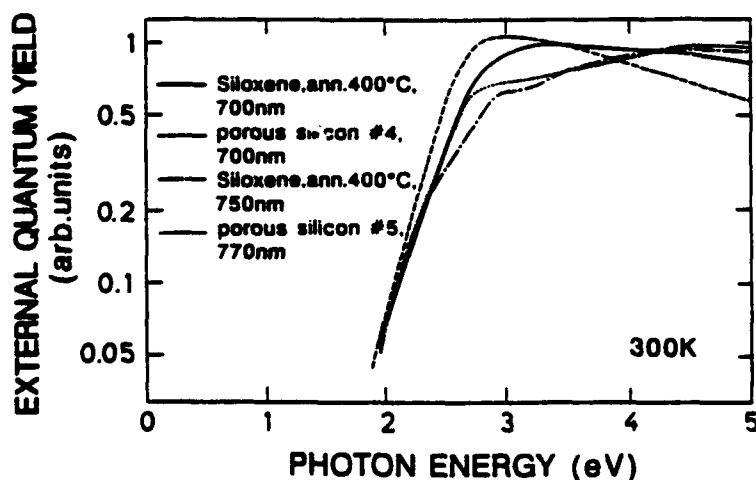


Figure 1: Comparison of the photoluminescence excitation spectra of two samples of porous silicon and of annealed siloxene at different monitoring wavelengths. All samples show the same characteristic exponential tail with a slope of 200 meV in the excitation spectra.

Experimentally, one observes a shift in the luminescence peak energy from typically 2.6 eV in as prepared siloxene to about 1.8 eV in the annealed substance. More dramatic changes occur in the photoluminescence excitation. While the luminescence of the as prepared siloxene can be excited resonantly, the spectra being very similar to those obtained for conventional direct bandgap semiconductors such as GaAs, the luminescence from annealed siloxene is best excited nonresonantly at energies above 3 eV (Fig.1).

Due to a variety of experimental results, we have previously made the observation that the luminescence from porous silicon can be traced back to siloxene-type  $\text{Si}_6$ -ring structures which are formed during the anodic oxidation process. This identification is based on striking similarities of annealed siloxene to porous silicon, in particular the position and shape of the luminescence spectrum, its similar dependence on laser intensity and temperature, the nonexponential luminescence decay with comparable decay times, identical ODMR spectra, similar pressure coefficients, the same degradation effect under UV illumination and common vibrational modes in IR and Raman spectroscopy. As an example, we compare in Fig. 1 the photoluminescence excitation spectra of annealed siloxene and of two porous silicon samples. Choosing the same monitoring luminescence wavelength, the respective excitation spectra of the two differently prepared materials are virtually undistinguishable.

Information on the microscopic signature of the luminescent transition can be obtained from optically detected magnetic resonance. The as-prepared siloxene shows a resonant enhancement of the luminescence efficiency with a Lorentzian lineshape (width 400 G). This is the signature of a well defined, delocalised excitonic state which is confined to the silicon layers. In both annealed siloxene and in porous silicon, the line changes to a Gaussian lineshape (again about 400 G width). Such a resonance (although with a smaller linewidth) is also observed in amorphous silicon and is believed to be due to disorder induced localisation. Further investigation of the optically detected magnetic resonance will yield valuable information on the nature of the luminescence from porous silicon.

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# Light-Emitting Siloxene Thin Films

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## Abstract

Siloxene structure was suggested as one origin of the light emissions from porous Si. We have deposited siloxene thin film by an evaporation method and observed its visible photoluminescence. We have also observed electroluminescence from the thin film at an onset voltage of 50 volts and a current density of 30 mA / mm<sup>2</sup>.

Siloxene structure was suggested as one origin of light emissions from porous Si.[1-3] In our previous reports, the light induced degradation, the temperature effect and the Staebler-Wronski like effect in siloxene were studied, and some comparisons to porous Si were made.[4-7]

The current electrochemical anodization method for porous Si has a drawback in making an applicable device, since the preparation method is not compatible with the planar processing. Siloxene thin film is desirable, if a conventional deposition method can be applied in the fabrication. Recently, the siloxene thin film made by MBE was reported, and it was claimed to have visible luminescence.[2]

Siloxene thin films deposited in our laboratory are obtained by a simple evaporation method. In our vapor deposition, powder CaSi<sub>2</sub> was used as the source in a high vacuum chamber of 10<sup>-6</sup> torr, and various Si substrates were used with different orientations and doping levels. The optimum substrate temperature was around 590 °C. Evaporation usually took about 15 to 30 minutes. The thin film obtained in this way was black. Then the film was dipped into the HCl + H<sub>2</sub>O solution for oxidation reaction. The oxidation chemical process was to replace calcium with the H<sub>2</sub>O group in the solution, which took about few hours at room temperature. The color of the thin film then turns green. The green to white luminescence can be seen by naked eye under a UV lamp.

Fig 1 show the photoluminescence spectra from two siloxene thin films. Two have slightly different preparation conditions. For the first thin film as shown in (a), the main luminescence peak position is at about 700 nm, and a shoulder is at about 550 nm. The second thin film has some different photoluminescence features: the high energy peak at 520 nm is developed and is larger than the 700 nm peak.

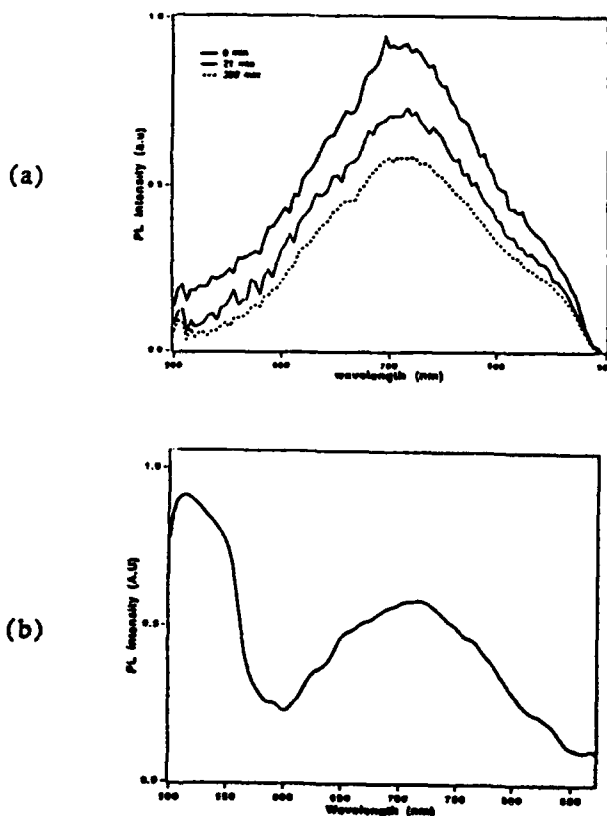
RBS data for the powder siloxene compound show the ratio of Si and O is 1:1. The analysis of the data from CaSi<sub>2</sub> film indicates the composition ratio was 0.5:0.9:1 for Si:O:Ca, and the film thickness was 600 nm. The analysis of the siloxene thin film indicates the composition ratio was 1:1.5 for Si:O, and the film thickness was 500 nm.

It is interesting to notice that we can also deposit a good thin film on an unpolished backside silicon. This may be an indication that the light emitting siloxene thin films need not to be single crystal. Ideally, siloxene has a planar layer structure, but it is likely that the deposition could lead to an amorphous phase. The light emission characteristics are expected to be preserved, even in this amorphous phase.

Electroluminescence from the above sample were also observed. While the I-V curve did show a diode characteristic, the orange color light emission started at a rather high voltage ( $> 50$  volts). The onset of the light emission accompanied a sudden voltage drop and a current density increase ( $30 \text{ mA/mm}^2$ ). This behavior is similar to a previous report on the porous Si electroluminescence. [8]

It is also important to notice that the light emission from the siloxene thin film has serious degradation under laser illumination, which is similar to what we reported previously for siloxene compound. While the detailed mechanism still needs to be worked out, it is conceivable that with depositing certain type of electrode for the contact, the degradation may also be avoided or minimized, and a stabilized state may be reached.

Fig.1  
Photoluminescence spectra from siloxene thin film deposited by evaporation method. The sample was at room temperature. Two samples (a) and (b) had slightly different preparation conditions.



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## PHOTOLUMINESCENCE FROM POROUS SILICON: A SURFACE-RELATED PHENOMENON?

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It has been suggested that visible light emission from porous silicon is the result of quantum size effects within the silicon band structure, and a variety of experimental results appear consistent with this model. However, some results are not as easily explained within this model, and it is these types of results which we would like to address.

First of all, low temperature (230°C-690°C) desorption of hydrogen from n and p-type porous Si (PSi) leads to a photoluminescence (PL) redshift as large as .35 eV, a gradual disappearance of the PL, and a loss of  $\text{SiH}_x$  structures<sup>1,2</sup>. A red luminescence can be recovered by a 1 second dip in an HF solution. Furthermore, no blueshifting of the PL peak in a variety of PSi samples was apparent with pore widening treatments, in which the porosity of the materials was increased from 20% to 60%.

Furthermore, cross-sectional microluminescence measurements of 70µm PSi samples show a continuous decrease of the red PL band intensity as a function of sample depth. The PL intensity decrease appears to be correlated with decreasing roughness of the structures, but no spectral shift is observed as a function of depth into the sample, indicating that the finer structures close to the surface do not exhibit a spectral shift. For samples annealed at 390°C, in addition to spectral intensity reduction, we observe the same redshift in all luminescence spectra independent of depth.

In addition, controlled continuous removal of silicon from the PSi by light oxidation does not result in a continuous PL blueshift, which would be expected in the quantum confinement model. Instead, the PL cycles repeatably between each oxidation/HF dipping cycle. Also, high temperature (1200°C) UHV anneals of PSi<sup>3</sup> leads to a collapse of the PSi structure, resulting in a material consisting of 100 - 200 nm silicon spheres, with very low dangling bond densities, similar to crystalline silicon. This material does not exhibit PL in the visible range but when dipped in HF for 2 seconds, strong visible PL in the red appears, with no structural changes noted ( $\text{SiH}_x$  complexes also appear).

The luminescence behavior of oxidized PSi at high temperatures has also been examined. No blueshifting of the photoluminescence has been noted with extended oxidation times (3 to 120 minutes), in a range where a 30% oxide thickness increase has been reported. This result again appears inconsistent with the quantum confinement model, since the luminescence energy does not appear to depend on particle size reductions.

Since much of this data appears to be inconsistent with the simple particle in a box quantum confinement model, one possible conclusion is that the visible red PL exhibited by PSi may be associated with a surface phenomenon, in which the polysilane/hydride complexes play a more significant role in the PL process than simple surface passivation. In this view, the PL energy may be a function of H content or specific  $\text{SiH}_x$  geometry on the surface, while the PL intensity is a function of total surface area.

<sup>1</sup> S.M. Prokes, O.J. Glembocki, V.M. Bermudez, R. Kaplan, L.E. Friedersdorf, and P.C. Searson, *Phys. Rev. B* **45**, (1992).

<sup>2</sup> S.M. Prokes, J.A. Freitas, Jr. and P.C. Searson, *Appl. Phys. Lett.* **60**, 3295 (1992).

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**IX. SUMMARY OF DISCUSSIONS**

## "Critical Issues in the Luminescence of Porous Silicon"

Summary of a Discussion Session at the International Workshop on Light Emission and Electronic Properties of Nanoscale Silicon, Charlotte, N.C., Feb. 2, 1993.

After three years of intensive work resulting from the initial reports of quantum phenomena in Porous Si (PS) by Gosele and Lehman, and by Canham, there is a consensus on some aspects: PS contains Si crystallites, and Si "wires" of undulating diameter, of < 5 nm size. Such small nanocrystals are theoretically predicted to show quantum size effects in optical absorption, luminescence, and in transport properties. PS does show quantum size effects in its optical absorption, in that the visible absorption spectrum shows a larger indirect gap than the bulk crystal. PS also shows visible luminescence that behaves as expected, with processing variables, for quantum confined emission from crystallites capped with either H atoms as initially prepared, or with a subsequently made, well formed (high temperature) oxide. As expected from simple confinement theory, the luminescence does shift blue when it appears that smaller crystallites have been made. The luminescence is anti-correlated with the magnitude of the ESR signal from dangling bonds, as expected if crystallite luminescence is in kinetic competition with nonradiative recombination at uncapped surface states (ie, dangling bonds). Excitation and luminescence spectra appear to show steps corresponding to the bulk TO Si phonon; this observation is evidence that the emitting species is a fragment of three dimensional diamond lattice silicon. Since strong luminescence experimentally is observed with passivation by either H or oxide, but does not require the simultaneous presence of hydrogen and oxygen, it is not likely that luminescence is due to specific molecular species such as siloxenes. Finally, there are independent studies of nanometer Si crystallites capped with oxide that report visible luminescence very similar to that of PS.

Much of the remaining uncertainty is related to the difficulty in physical characterization of PS. No study has yet clearly shown which crystallites, wires, or "amorphous region" is actually emitting in this extremely heterogeneous material. Presently we can not exclude the possibility that some types of PS may have a luminescence mechanism in addition to the passivated wire and crystallite mechanism.

The above observations qualitatively seem to imply that the PS visible luminescence involves quantum confined luminescence. However, a quantitative understanding, and even a qualitative understanding of some basic observations, is presently lacking. It

is not clear yet whether the photoluminescence decay kinetics primarily reflect dynamics within one crystallite, or coupling (of energy and/or carriers) between crystallites. For example, the commonly observed decrease of the steady-state photoluminescence at temperatures below 200 K could be due either to a singlet-triplet fine structure in the emitting state within one crystallite, or due to thermally activated transport of carriers from one crystallite to the next. It is also not clear yet whether the emitting state corresponds to both electron and hole in the lowest particle-in-a-sphere quantum confined state, or whether one (or both) carrier is in some sort of surface localized state. It has not been shown yet whether the apparent quantum confinement increase in luminescence efficiency is purely electronic, or is due to the size dependence of electron-phonon coupling. In resolving all these questions, it would be very helpful to have photoluminescence excitation and emission spectra for essentially monodisperse crystallites as a function of size.

In the realm of theory, a number of questions remain outstanding: what is the expected fine structure due to valley-orbit splitting and spin degeneracy, in various crystallite geometries? How fast do hot electrons relax when three dimensional confinement is present? Does the intrinsic nature of the Si/oxide interface support localized surface states, on particles, that might give radiative recombination? What is the thermodynamic equilibrium structure of an oxide capped particle as a function of size? Alternately stated, what does the phase diagram between Si and O look like when finite size effects and surface energies are included? How far can the luminescence be shifted to higher energy before the diamond lattice structure of the confined crystallite changes? Is the oxide cap stable against photochemistry, and carrier induced chemistry, at 1 eV confinement energies?

In the area of electroluminescence, several outstanding questions remain: How can we understand transport through a disordered "sponge" of Si wires? Can we find a "fluid" electrical contact that will penetrate the pores and allow efficient charge injection into PS without structural degradation? What is the macroscopic junction physics of a fluid contact to a porous thin film?

Summary prepared by Louis Brus, AT&T Bell Laboratories, Murray Hill, N.J.

### Discussion Session: Critical Issues of Electrical Transport in Nanoscale Silicon Structures

The discussion session started with additional questions on the paper by E. Nicollian *et al.*

**Q:** Why are the I-V characteristics of your samples so sharp?

**A (Nicollian):** The speculation is that the particle size is uniform and spherical, due to minimization of the free energy. The poly deposition constrains the particle size to a diameter comparable to the thickness of the film. Of course, the spacing of particles varies. The size of the crystallites also depends on the substrate temperature; you can also make the particles larger by heating afterwards.

The discussion then focused on electronic transport in porous silicon.

**Comment:** An interesting experiment is to compare conductivity perpendicular to the columnar structures versus conductivity parallel to the columns. This has implications as to the microstructural model of the porous silicon; whether they are small silicon microcrystallites encased in the columns or not. So far, no one knows of, or has measured, any anisotropy.

**Comment (Koch):** An important point is that the transport is basically activated. If you measure conductivity versus temperature over a wide range of temperature, you get that the transport is indeed thermally activated, with a huge activation energy, of about 1/2 an electron volt. There are no free carriers in the structure - it's fully depleted. The resistivity of these films are approximately  $10^{10}$  ohm-cm. So what's this from? The activation energy is consistent with the "kidney" model. Has anyone else measured a similar energy?

**A:** We get half a volt.

**Comment (Koch)** That agrees well with our measurement of 0.6 eV.

The discussion then turned to STM measurements.

**Comment:** STM of these films is very difficult. You try to image the films, and the variation in resistance causes the tip to crash. We don't know yet how to solve this.

Finally, the session concluded with a list of transport important experiments to do:

- measure the percolation limit.
- determine the origin of the ~1/2 eV activation energy. What is the model to explain this?
- pursue STM measurements. What is the best approach?

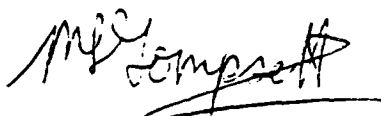
Prepared by Mark Reed, Yale University

I thank you for the opportunity to visit UNCC and meet some familiar faces. TSU's workshop was a model of focus, interactive discussion and ideas. This moderator enjoyed his discussion session but has no intention of writing two pages about it (!), but here is a paragraph.

I made the point that the structures under discussion fall into two categories, the accidental (e.g., porous silicon), which can be fabricated very inexpensively, and the deliberate, which require expensive micro-fabrication technologies. There were three (3) people in the audience who appeared responsive to the issue of applications of these structures. These were Matsumoto, who is interested in low cost electro-luminescence panels, e.g. for low power room illumination, and Nanovar, from Spire, and another guy sitting behind him, who picked up on the issue of clock synchronization in large silicon chips. With respect to the silicon application and, interesting suggestion was made that the emission from porous silicon had a sufficiently long silicon wave length that it could penetrate the silicon substrate but then be detected by a doped photo-diode on the front surfaces of the chip.

Clearly the technology and the majority of the audience were a long way from being ready for these applications.

I wish you all the best.

A handwritten signature in black ink, appearing to read "M. F. Tompsett", with a stylized flourish at the end.

Michael F. Tompsett  
Director-Electronic  
Devices Research Division



## **What Role Could Nanoscale Si play in Silicon Devices?**

### **Discussion Session**

A number of suggestions were made during the course of the workshop regarding possible uses for nanoscale Si in device applications. This question can be approached both from the standpoint of asking what role quantum confinement in general can play in altering and controlling electrical and optical properties for improved devices, as well as the specific issue of porous silicon as a relatively low cost, high volume means for the production of quantum confined silicon. Among ideas suggested were 1) use of porous silicon for small, low cost optical displays, 2) visible and IR LEDs, 3) sensors utilizing the surface sensitivity of porous silicon, 4) anti-reflection coatings, 5) optical interconnects and switches and 6) digital circuits (most probably based on more controlled fabrication techniques). The idea of a low cost "Si retina" was also proposed.

Discussion on these topics centered on issues of stability and speed of the luminescent mechanism. Several groups reporting room temperature electroluminescence said that their most recent devices did not show degradation during periods of operation ranging from hours to days, though no definitive long term results were presented. If the stability problem is not an issue, this raises hopes for the development of low cost optical displays where speed is not an issue. The relatively long lifetime associated with the dominant visible luminescence appears to be a major stumbling block in many possible interconnect and switching applications.

Major issues to be addressed in the applications area include a better understanding of transport properties, development of contacting schemes and the development of stable passivating surfaces. Recent results on the high temperature oxidized porous silicon may be useful in this regard.

Most of the applications discussion focused on whether porous Si could be used - perhaps more efficiently, cheaply, widely, easily, etc. - in device applications that are already in use or under development with other materials. One could also ask whether the very low cost and ease of fabrication, as well as other important mechanical properties of silicon, might

also lead to the use of porous silicon and semiconductors in optical applications where they are presently not considered for use at all. The integration of porous Si with the Si-based micro-machined devices currently being pursued is one interesting possibility. It may also have applications where UV light needs to be filtered or down-converted to the visible spectrum. Porous Si may give a whole new meaning to the phrase "rose-colored glasses."

Nancy M. Haegel

The tape from the discussion section was not available for the preparation of the summary, so individual remarks cannot be reviewed.

## CHARLOTTE STANDARD

Following Prof. F. Koch's suggestion of establishing a "Charlotte Standard", to facilitate comparison of luminescence efficiency, a special discussion session was devoted to this subject. The following suggestions represent some possibilities:

- 1) L. Brus proposed the use of Rhodamine G dye with a concentration below lasing threshold as a source of luminescence for calibration purposes.
- 2) J. C. Vial proposed that luminescence life times should be sufficient for standards.
- 3) R. Lux proposed to use a diffuse - surface such as magnesium oxide as a standard.
- 4) B. Delley pointed out the ultimate need to obtain external quantum efficiency. (Giving the porous nature of the material, most people thought that quantum efficiency may not be meaningful)
- 5) O. Glembocki proposed to use other materials such as GaAs as a standard.

At the time of the discussion, the use of a dye as a standard seems to be preferred. However, it was pointed out later that dyes do degrade. There wasn't any agreement on a standard!

Prepared by R. Tsu

## What have we learned and how do we proceed?

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This workshop has demonstrated that light emission from silicon nanostructures is at least an important new development in science and may also lead to technological applications, provided that some specific improvements are made. Although some issues are not yet closed and some controversies remain, a consensus is emerging. In what follows, I propose a summary of what we have learned since 1990 and of how to proceed, with a special emphasis on porous silicon.

### WHAT HAVE WE LEARNED?

Visible light emission from silicon depends on at least two factors: crystalline nanostructures on a length scale  $\leq 5$  nm, and good surface passivation. Work on porous silicon and silicon nanoclusters indicates that efficient light emission requires extremely small nanoparticles and that the peak photoluminescence energy increases with decreasing particle size. These observations are in general agreement with the quantum size model, although they cannot be taken as a proof for it. Surface passivation, by hydrogen and more recently silicon dioxide, eliminates most of the dangling bonds which would suppress the luminescence by providing a channel for non-radiative recombination. It now seems very unlikely that the surface properties govern the luminescence, although it must be pointed out that modifying the surface chemistry can provide in some cases a substantial change of the luminescence properties. Progress in the past year has been substantial and can be summarized as follows:

- 1) the controversy regarding the species responsible for luminescence (siloxene, silicon hydride, amorphous silicon, crystalline silicon nanocrystals), although not yet completely settled, is fading away in view of mounting evidence for a "hybird" model (see point 6)
- 2) the stability of the photoluminescence has been improved by orders of magnitude.
- 3) the highest reported quantum efficiency for a porous silicon LED is  $>10^{-4}$  at 300 K.
- 4) luminescence occurs not only in the red-orange part of the visible spectrum, but also in the blue and in the near infrared, although the properties of these PL lines are very poorly known.
- 5) light emission has been obtained from many different forms of silicon, from porous silicon to silicon nanoclusters, Sig cubes, silicon-based polymers, and siloxene, with characteristics having a lot in common.
- 6) in addition to many excellent calculations of the bandgap of silicon wires and clusters, which may or may not be directly relevant to light emission from the complex structures found in porous silicon but do indicate an opening of the bandgap and a dramatic decrease of the radiative lifetime with decreasing size, a first attempt at a more realistic and comprehensive model for light emission in porous silicon has been made. This model considers surface and trap states in addition to the opening of the gap due to quantum size effects. At this point in its development, this model has no concrete predictive power yet.

### WHAT DO WE NEED TO LEARN?

To improve our understanding of porous silicon, three specific areas of research should be emphasized:

- 1) develop theoretical models that predict physical phenomena on a nanometer scale.
- 2) develop new growth and processing techniques to control the desired properties.

3) use better characterization tools.  
I now examine each of them in some detail.

The mesoscopic scale is the most difficult to model in physics, because many concepts developed for infinite translational symmetry break down and yet the number of atoms involved is large enough that precise cluster-like calculations are nearly impossible. In general, it would be useful to determine when the concepts that come from solid state physics (e.g., effective mass) must be replaced by concepts coming from chemistry. A list of unresolved issues includes: (i) a reliable description of the electronic properties (including band structure and wavefunctions); (ii) a theoretical description of defects in constricted geometries (as opposed to bulk or flat surfaces); (iii) a proper description of the phonons (bulk and surface modes); (iv) a detailed model for the dielectric function and the binding energy of dopants in nanostructures.

The most popular model for the formation of the nanostructures in porous silicon during electrochemistry naturally leads to a relatively narrow size distribution, because etching stops when holes supplied by the substrate can no longer overcome the valence discontinuity at the crystalline silicon-porous silicon interface. This self-regulation leads to a material that cannot be described as a fractal. Size uniformity is not necessary to obtain photoluminescence, since it appears that light will only be emitted by particles of size  $\leq 5$  nm. However, size uniformity could lead to a narrower photoluminescence linewidth and to photoluminescence efficiencies well in excess of 10%, which is the best ever reported so far for porous silicon at 300K. Also, size fluctuations within a singular structure (the "undulating wire" model) implies poor connectivity and poor conductivity, which is important for electroluminescent devices. It appears that lithography could minimize the uniformity problem; unfortunately, for size well below 10 nm, it is an extremely difficult and expensive technique, and thus probably not the way to proceed at this time. Possible solutions might include new, clever chemical syntheses, or assisted electrochemistry. Any technological relevant technique should lead to a high density structure.

There is also a need for better characterization tools. Most of the knowledge we have gathered on porous silicon has come from macroscopic tools. However, as porous silicon is a heterogeneous material on a nanometer scale, it would be highly desirable to characterize it with tools capable of comparable spatial resolution. The most prominent example of such tools is the scanning tunneling microscope. Positive correlation between any given type of nanostructure and light emission is needed. In addition, one should strive towards the development of a more sophisticated analysis of conventional characterization techniques that would take into account the composite nature of porous silicon.

### SPECIFIC GOALS

Finally, a list of short term ( $\leq 1$  year) and long-term ( $\geq 1$  year) goals has been established. The short term goals include: (i) verify the validity of the hybrid model; (ii) determine the origin of the blue and infrared luminescence lines; (iii) determine what controls the luminescence linewidth; (iv) learn how to minimize degradation and agree how much is acceptable for future device applications; (v) improve the mechanical stability of porous silicon; and (vi) establish the carrier dynamics and the radiative lifetime, from picoseconds to milliseconds.

The long term goals include: (i) establish the conditions for high efficiency and fast photoluminescence and electroluminescence; (ii) achieve size and shape control; (iii) take steps towards defect engineering, either to avoid them or to take advantage of them; and (iv) achieve high quality, long-lived solid state electrical contacts for LEDs.

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